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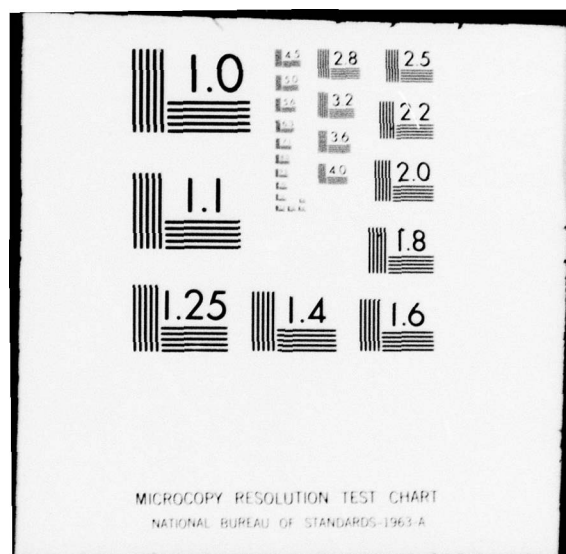
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OVERAGE INDICATOR FOR GRAPHITE FIBER EPOXY

Z. N. Sanjana  
Principal Investigator

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Final Report for the Period  
15 June 77 to 14 June 78  
Contract No. N00019-77-C-0247 *new*

June 1978

Department of the Navy  
Naval Air Systems Command  
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Z. N. Sanjana

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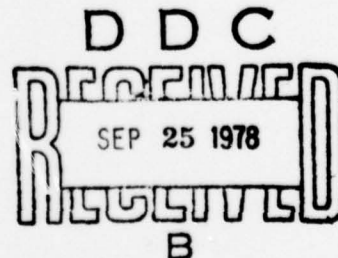
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Block No. 20 (Abstract)

Prepreg or B-staged products are used extensively in the aerospace, electrical, and communications industries. They consist of a partially reacted mixture of monomers which have been impregnated into the reinforcement. During shipping and storage, prior to use, the reactions will continue. The amount of reaction or 'age' of the prepreg will depend on the conditions (principally, temperature and time) that it has been exposed to. These conditions are often unknown. At a point in the age of the prepreg, some critical property or properties will deteriorate. This would then represent the end of the useful life of the prepreg. The critical property will often depend upon the material and the end use intended of the prepreg. The overage indicator may then be the critical property itself or some other measurement which tracks the age of the prepreg and correlates well with the loss of the critical property. The latter affords more flexibility and generality of application to many products.

It is particularly necessary to know the age of the prepreg if it is to be used under field conditions (such as on a base or on a carrier) to effect repairs to a composite structure. In such situations, the prepreg is used only intermittently and long periods of storage are possible. Exhaustive testing of the prepreg prior to use is not feasible and an overage indicator would be most useful. A simple overage indicator would obviously have the greatest advantage for field use whereas a more complex, rigorous test would be more appropriate for in-plant use. Both types of indicators were investigated.

This report provides data and results of aging studies performed on Hercules 3501-6/AS graphite epoxy prepreg. Diverse conditions of temperature and humidity were used including intermittent exposure to different temperatures. At various times during the aging, physical properties of the prepreg were measured, and mechanical properties of laminates made from aged prepreg were obtained. During the aging, the following methods were used to track the age of the prepreg: (1) dielectric analysis (DA), (2) dynamic mechanical analysis (DMA), (3) differential scanning calorimetry (DSC), and (4) a simple, easy to use time-temperature integrating device (TTW) which is carried with the prepreg and provides a visual observation of the time and temperature exposure of the prepreg.

It was found that DA, DMA, and the TTW can be used to follow the age of the prepreg and that they can be used as overage indicators to tell the user that the prepreg has lost its useful life. Some data on chemical changes during aging is also presented.

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# FOREWORD

The following final report describes work performed on NASC Contract No. N00019-77-C-0247, "Overage Indicator for Graphite Fiber Epoxy". The work accomplished and reported herein was performed by Westinghouse Electric Corp., R&D Center, except where specifically noted. The program was administered by M. Stander for the Naval Air Systems Command.

The program was conducted in the Polymers and Plastics Department, J. H. Freeman, Manager, with Z. N. Sanjana as principal investigator. Contributions to the program were also made by J. L. Hammill and R. L. Selby.

This report covers the contract period 15 June 1977 to 14 June 1978.

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## 1. INTRODUCTION

The use of non-metallic materials for structural applications in high performance military aircraft is increasing. The principal non-metallics used are advanced composites and adhesives. The advanced composite material (usually graphite-epoxy) for structural application is generally obtained from the supplier as a prepreg or a B-staged product.

A prepreg product consists of a partially reacted mixture of monomers which has been impregnated into the reinforcement. During shipping and storage, prior to use, the reactions will continue. The amount of reaction or "age" of the prepreg will depend on the conditions (principally, temperature and time) that it has been exposed to. These conditions are often unknown. At a point in the age of the prepreg, some critical property or properties will deteriorate. This would then represent the end of the useful life of the prepreg.

An overage indicator should reliably inform the user of a prepreg when its useful life is over. This requires that the useful life of the prepreg be defined. With an epoxy system, this often depends on the end use for the prepreg. If the user is only interested in making flat laminates, for example, the prepreg can be used well after the point at which it becomes stiff and boardy. If, however, the use requires laying up the prepreg in a complex shape, it must be soft and tacky so that it can be draped and it can adhere to itself. In general, the end point of the useful life of a prepreg occurs when some critical property begins to be adversely affected. The critical property concerned will depend upon the end use intended for the product.

The overage indicator then may be either the critical property itself or some other measurement which correlates well with the loss of the critical property. The latter affords more flexibility and generality of application since, as observed above, the critical property could change depending on the material and the end use.

It is particularly necessary to know the age of the prepreg if it is to be used under field conditions (such as on a base or on a carrier) to effect repairs to a composite structure. In such situations, the prepreg is used only intermittently and long periods of storage are possible. Exhaustive testing of the prepreg prior to use is not feasible and an overage indicator would be most useful. A simple overage indicator would obviously have the greatest advantage for field use whereas a more complex, rigorous test would be more appropriate for in-plant use.

This report describes aging studies that were carried out on one product - Hercules 3501-6/AS graphite-epoxy prepreg. Several methods that successfully track the age of the prepreg are described. These are: dielectric analysis (DA), dynamic mechanical analysis (DMA), chemical analysis and a time-temperature integrating indicator (TTW). Differential scanning calorimetry (DSC) of the prepreg was also studied.

The methods studied here are of general application and should prove useful to study the aging characteristic of any product that may result during shipping and storage. These methods may also be useful in setting up QC/QA controls on incoming material as well as on stored material.

## 2. SUMMARY

The method used in this study was to determine (for a given material) that critical property which is the first to deteriorate when the material is aged in shipping, storage, and handling. Various techniques are then used to track the aging of the prepreg under diverse storage conditions. The results obtained are correlated to the deterioration in the critical property. Thus each technique provides a number (or value) which is then used as a decision point to reject that lot of material as having exhausted its useful life.

Under the present contract the material examined was 3501-6/AS graphite prepreg supplied by Hercules Inc., Magna, Utah. It was determined from our aging studies that the critical property that first deteriorates on aging is tack. This was also confirmed by the supplier.

During the course of the study, samples of the 3501-6/AS prepreg were obtained from the supplier. The prepreg was subjected to several aging conditions:

- Freezer storage (-4°F)
- Room ambient (72-78°F, 30-65% RH)
- 120°F
- 120°F, 95% RH
- Intermittent exposure from freezer to 120°F, 80% RH
- Intermittent exposure from freezer to room ambient.

During these aging periods, the following tests were performed:

### Tests of Age Indicators

- Time Temperature Integrator: Several types of indicators (from one supplier) were obtained and exposed to the same aging conditions as the prepreg. The purpose was to see if under diverse aging conditions, the devices would track the age of the prepreg and would provide a number which would correlate with the loss of the critical property.

- Dielectric Analysis (DA): During the aging, at periodic intervals, measurements were made on the prepreg using an automatic dielectrometer. The measurements were made under dynamic temperature conditions to obtain

the temperature of the relaxation peak in dissipation factor, and under isothermal conditions to obtain the isothermal time to peak in dissipation factor.

- Differential Scanning Calorimetry (DSC): At periodic intervals during aging, DSC scans were made to obtain the temperature of the peak exotherm and the residual heat of exotherm.

- Dynamic Mechanical Analysis (DMA): While the original contract did not call for any DMA work, it was included in the program because of the indifferent DSC results. At periodic intervals during the aging, the temperature of the relative damping peak was obtained using a dynamic mechanical analyzer.

#### Physical Properties of the Prepreg

During the aging study, at periodic intervals the resin flow and prepreg tack were measured.

#### Mechanical Properties of Laminates

Periodically, laminates were press molded from the aged prepreg. The flexural strength, flexural modulus, and interlaminar shear strengths of the laminates were measured.

#### Chemical Changes

While we did not propose nor perform chemical analyses on the prepreg, Dr. G. Hagnauer of the Army Materials and Mechanics Research Center performed a series of experiments on the 3501-6/AS prepreg as it aged at room ambient. By using liquid chromatography and Fourier transform infrared analysis, they were able to show changes in the chemical composition with the age of the prepreg. Their data is also presented here with their permission.

### 3. EXPERIMENTAL

#### 3.1 MATERIALS

The aging behavior of only one material was investigated in this period. This is the Hercules 3501-6/AS prepreg. It consists of unidirectional "A" type graphite fiber which is impregnated (without solvent) with an epoxy resin mixture which is only slightly B-staged. While the supplier will not disclose the precise constituents of the matrix, this much is known<sup>(1)</sup>: It consists of three epoxides of which one is principal. The curing agent is diaminodiphenyl sulfone and the catalyst is a  $\text{BF}_3$  complex.

During the course of the year, three batches of prepreg were obtained from the supplier. Normal shipping channels were used and no special handling was given. Hercules was asked to activate and include several TTWs with each shipment. For the purposes of this report, the three batches obtained are labeled F, FN and FA. If not otherwise stated, the data presented is for the F batch. Table 1 presents information on the three batches of material as given by the supplier. Note the resin contents of the three batches. F and FN have the standard resin content. FA is a special low resin content grade which is being supplied to McDonnell Aircraft. The FA batch was obtained in April 1978 to verify what effect the lower resin content might have on our studies. DA and DMA results on this batch are reported here. Laminates made during the aging will be tested for their mechanical properties during the next phase.

TABLE 1  
BATCHES OF 3501-6/AS PREPREG USED IN THIS STUDY

Batch ID	Hercules Lot and Spool No.	Resin Content (%)
F	597 4H	42
FN	612 3C	41
FA	791 2A	35

### 3.2 TIME-TEMPERATURE INTEGRATOR

The time-temperature integrating and indicating device used in this series of experiments is called Time/Temperature Watch (TTW) and is supplied by the Info-Chem Div. of Akzona, Inc. Another such device called the Monitormark is made by the 3M Co. This product was not evaluated during this reporting period, but an evaluation is planned for the next.

The time-temperature watch (TTW) supplied by Info-Chem is a strip of sensitized paper with numbers running from 1 to 10. After the TTW is activated (by breaking a small glass ampule) a color change appears on the sensitized strip and with increasing time or temperature the color change advances along the strip from 0 to 10. Thus the scale reading integrates the time and temperature to which it has been exposed. Several TTWs are available to cover a range of times and temperatures. They are listed in Table 2. Figure 1 shows a photograph of a TTW before and some time after activation.

TABLE 2  
TIME-TEMPERATURE WATCHES CURRENTLY AVAILABLE

<u>Type</u>	<u>Application</u>	<u>Characteristics</u> <u>(Full Scale Reading)</u>
#21	Freezer storage	2.8 days at 10°C 1.2 days at 20°C 0.5 days at 30°C
#27	Refrigerated storage Freezer storage	16 days at 0°C 5.7 days at 10°C 2.4 days at 20°C
#30	Refrigerated storage Long-term freezer storage	92 days at 0°C 29 days at 10°C 8.4 days at 20°C 2.8 days at 30°C
#33	Refrigerated storage Ambient storage	95 days at 20°C 19 days at 30°C 6.3 days at 40°C
#39	Longer term ambient Storage & shipping	67 days at 30°C 15 days at 40°C 5 days at 50°C

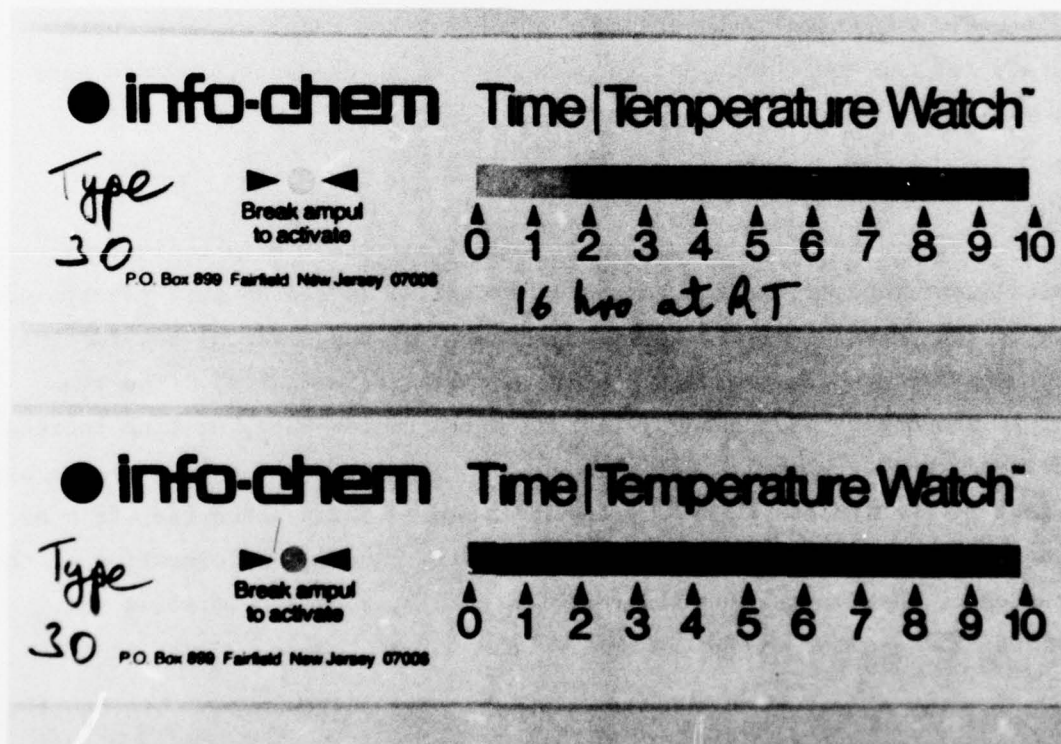


Fig. 1 - Type 30 TTW before and after activation. Advancing color change along the strip gives the value of the reading.

Appendix A presents some literature from the supplier giving the product description and the procedure to activate the TTW. The supplier also provided graphs which related the time and temperature of exposure to scale readings of the TTW for each type of TTW listed in Table 1. An example of the graph for the Type 33 TTW is given in Appendix A.

Our experience with the TTWs indicate that the readings are repeatable within  $\pm 1/2$  of a unit of scale reading when exposed to the same conditions. In general, the graphs provided by the supplier were quite accurate for the conditions and temperatures we checked out, provided very high humidities were not encountered.

### 3.2.1 Aging Behavior of the TTWs

After the glass ampule is broken (i.e., the TTW is activated), the chemical contained within the ampule (chemical A) is stored in a plastic pouch which is the primary barrier against diffusion of the chemical towards the indicating strip which contains another chemical (chemical B). The two react to produce a color change. At any given temperature, as time increases, more and more of chemical A diffuses out of the plastic pouch and reacts with chemical B, thus producing a progression of color change down the strip as shown in Figure 1. Increasing temperature will cause an acceleration of the diffusion of chemical A, and its reaction with B, thus accelerating the movement of the color change.

Most of our work was done with the Type 33 TTW because it has the appropriate range of time at ambient and above ambient temperature for use with the 3501-6/AS prepreg. Figures 2 and 3 show the behavior of the Type 33 under different aging conditions. Figure 2 shows the behavior under ambient conditions. The continuous exposure was under a slightly higher average temperature and higher relative humidity. The intermittent exposure was carried out during the winter and spring when the relative humidities and temperatures were lower. The readings are quite close (within about  $1/2$  unit) and do not show any effect of humidity differences. However, very high humidities retard the progression of the color change as shown by Figure 3. It shows curves for continuous and intermittent exposure of the Type 33 TTW to  $120^{\circ}\text{F}$  at

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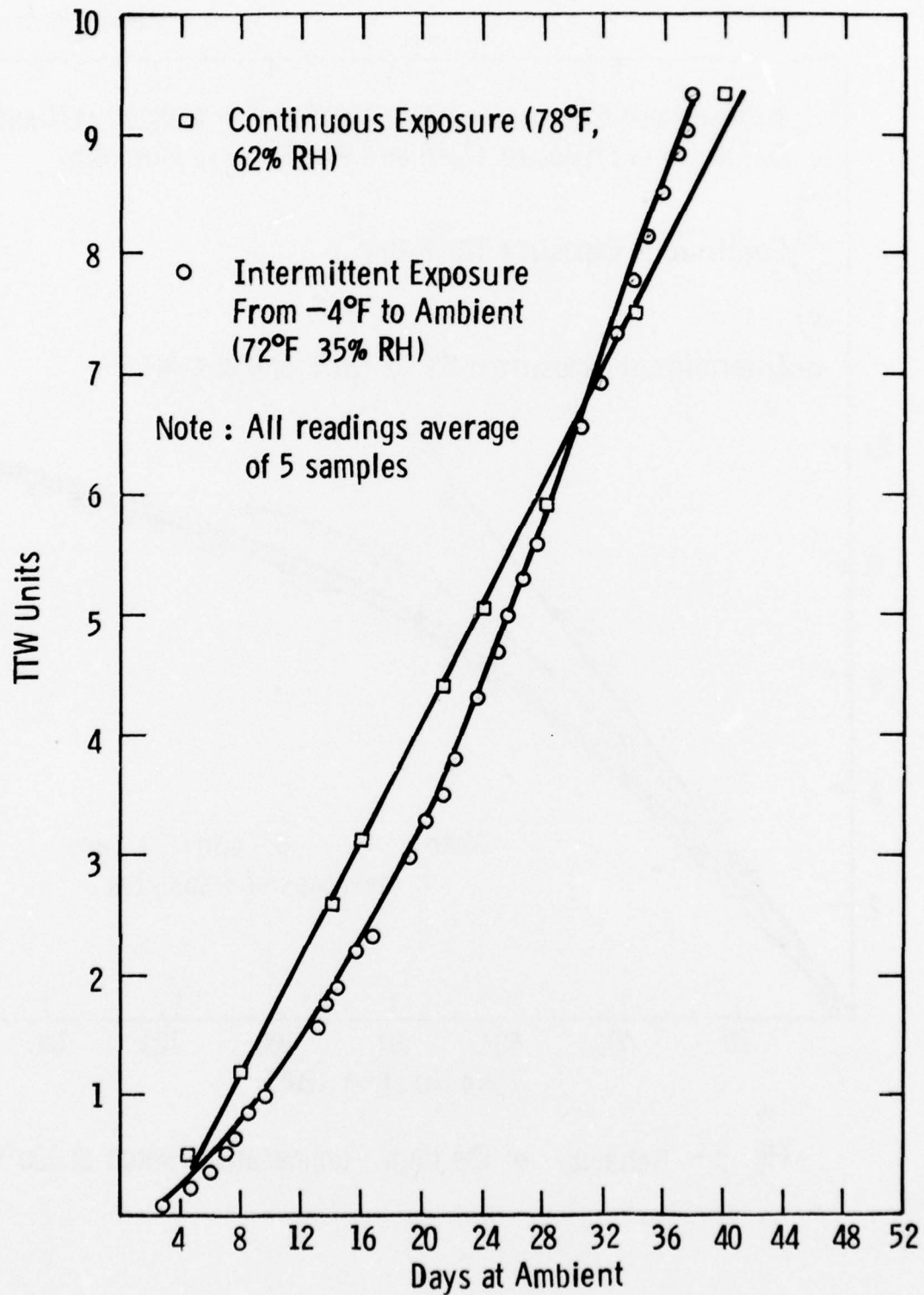


Fig. 2— Behavior of Type 33 TTW at ambient conditions

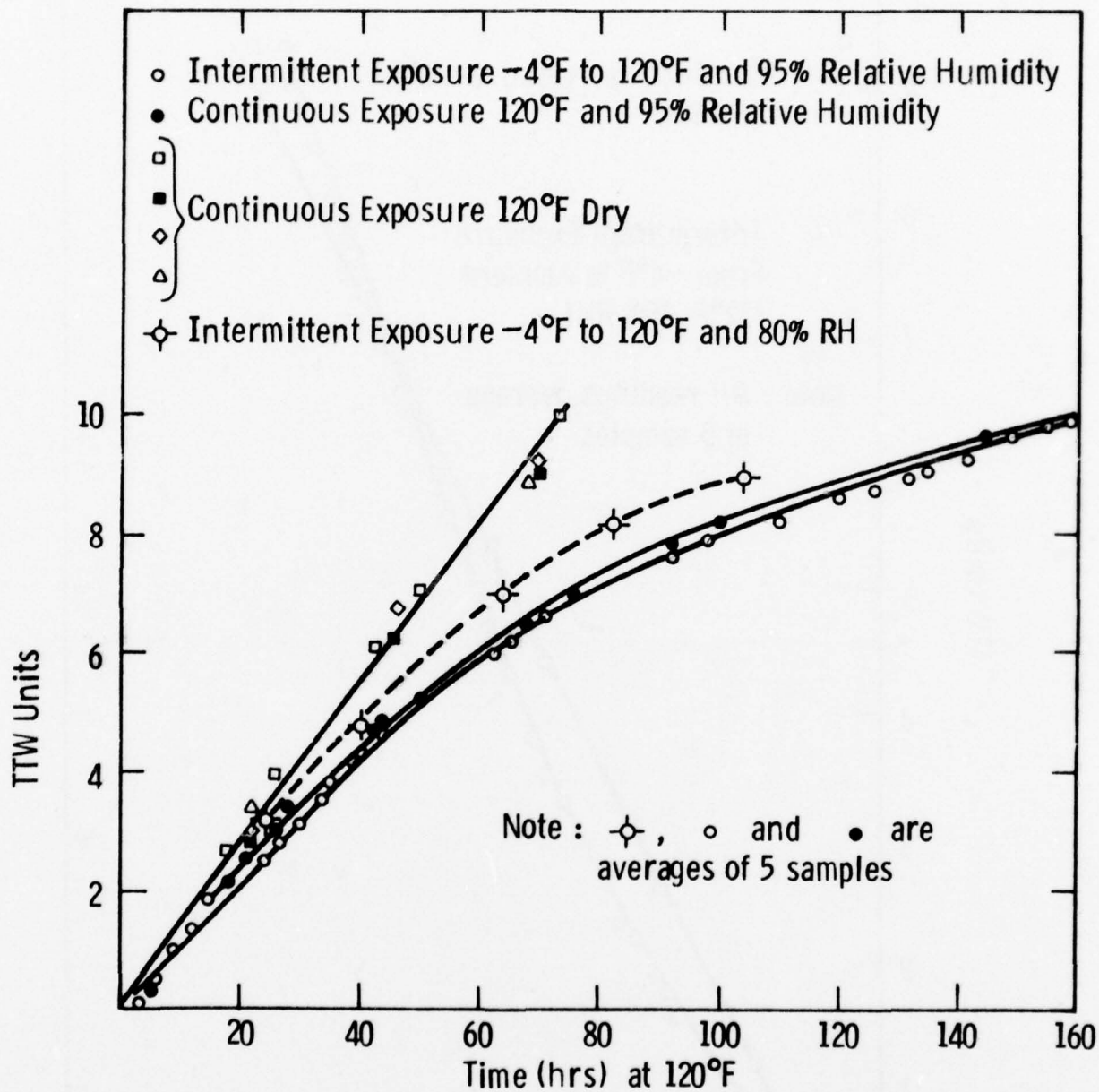


Fig. 3 - Behavior of T33 time - temperature watch at 120°F

95% RH, 80% RH, and dry. In the range of 30-80% RH that may be typically encountered, the differences at high ambient temperatures ( $\sim 120^{\circ}\text{F}$ ) are unlikely to exceed  $\pm 1/2$  unit. The effect of high humidity (80% RH) at lower temperatures is planned for investigation.

The purpose of the intermittent exposure studies shown in Figures 2 and 3 was to simulate the removal and exposure of the prepreg from the freezer to use conditions and replacement in the freezer. Intermittent exposures do not produce any deviations from results of continuous exposures.

Preliminary data on the effect of UV radiation on the TTWs indicate that serious fading of the color takes place after 4 hours in a Fadeometer at  $120^{\circ}\text{F}$  which is set to simulate noon, summer sunlight in Chicago. This is unlikely to be a serious problem because outdoor exposure of the prepreg or the TTW is unlikely. In other applications where such exposure is likely, the TTW can be easily protected by placing it in an opaque pouch.

### 3.3 DIELECTRIC ANALYSIS (DA)

Dielectric analysis (DA) utilizes the polar groups that are present in a thermosetting resin to indicate its state at any time in its processing history. A dynamic electrical stress - an ac voltage - is applied to the sample. The dipoles present in the resin respond to this stress by attempting to align themselves with the field. Since these polar groups are attached to other molecules, their mobility is restrained. During polymerization, there results an ever increasing restraint on dipole mobility, thus the response of the resin sample to the applied dynamic electric field changes with the course of the reaction. Interpretation of these changes allows one to measure the degree of B-staging and the degree of cure of the polymer.

The response of a polymer to an applied ac voltage can be measured by any ac bridge, but the use of a self-balancing bridge with an automatic readout which can be plotted continuously is most convenient. Such a machine is called an automatic dielectrometer, or by its acronym, Audrey. Hence, the technique of dielectric analysis is often referred to in the literature as automatic dielectrometry. In DA, the polymer responses measured are dissipation factor ( $\tan \delta$ ) and capacitance (C).

The theory and use of dielectric analysis in following the progress of polymerization, characterizing the degree of B-staging (i.e., tracking the age of prepreg), and characterizing the degree of cure of composites has been reported in detail by this author.<sup>(2)</sup> In brief, two methods may be used to characterize the degree of B-staging or age of a resin system relative to some initial state.

In the first, the sample (prepreg or aged resin mixture) is heated at some constant rate while its dissipation factor is continuously monitored at a given frequency. It is found that at some temperature, the dissipation factor goes through a maximum. This peak in dissipation factor is the relaxation peak associated with the softening or flow of the resin. If a resin ages during storage or use prior to full cure (i.e., it continues to react), then the temperature of this softening or flow will increase. Consequently, the temperature of the first relaxation peak in dissipation factor at a fixed frequency will increase. This is shown in Figure 4 for the 3501-6/AS prepreg for the 120°F aging series. The peak for unaged prepreg is at 50°C and the temperature of the peak increases with age. The temperature of the peak can then be used to characterize the prepreg age. May, Hadad, and Browning<sup>(3)</sup> have reported a similar shift in the temperature of the peak in dissipation factor with age for an unidentified epoxy prepreg.

The second is an isothermal procedure. A suitable test temperature and frequency are selected and the time taken for the dielectric relaxation peak (the peak in the dissipation factor) to appear is measured. The occurrence of the peak is the result of the material achieving a dielectric relaxation time corresponding to the observation frequency. For a given temperature and chemical system, the dielectric relaxation time is a function of molecular weight or of the conversion to polymer that is achieved by reaction up to that point. Thus, a prepreg that is more advanced will result in the appearance of a relaxation peak earlier in time during the reaction. This is shown in Figure 5 for 3501-6/AS prepreg, at 180°C and 1.0 kHz. As the prepreg is aged, the time to peak diminishes from 16 mins for unaged prepreg to 11 mins for prepreg aged 18 days at 120°F. The shift in time to peak is analogous to changes that would be expected in the gel

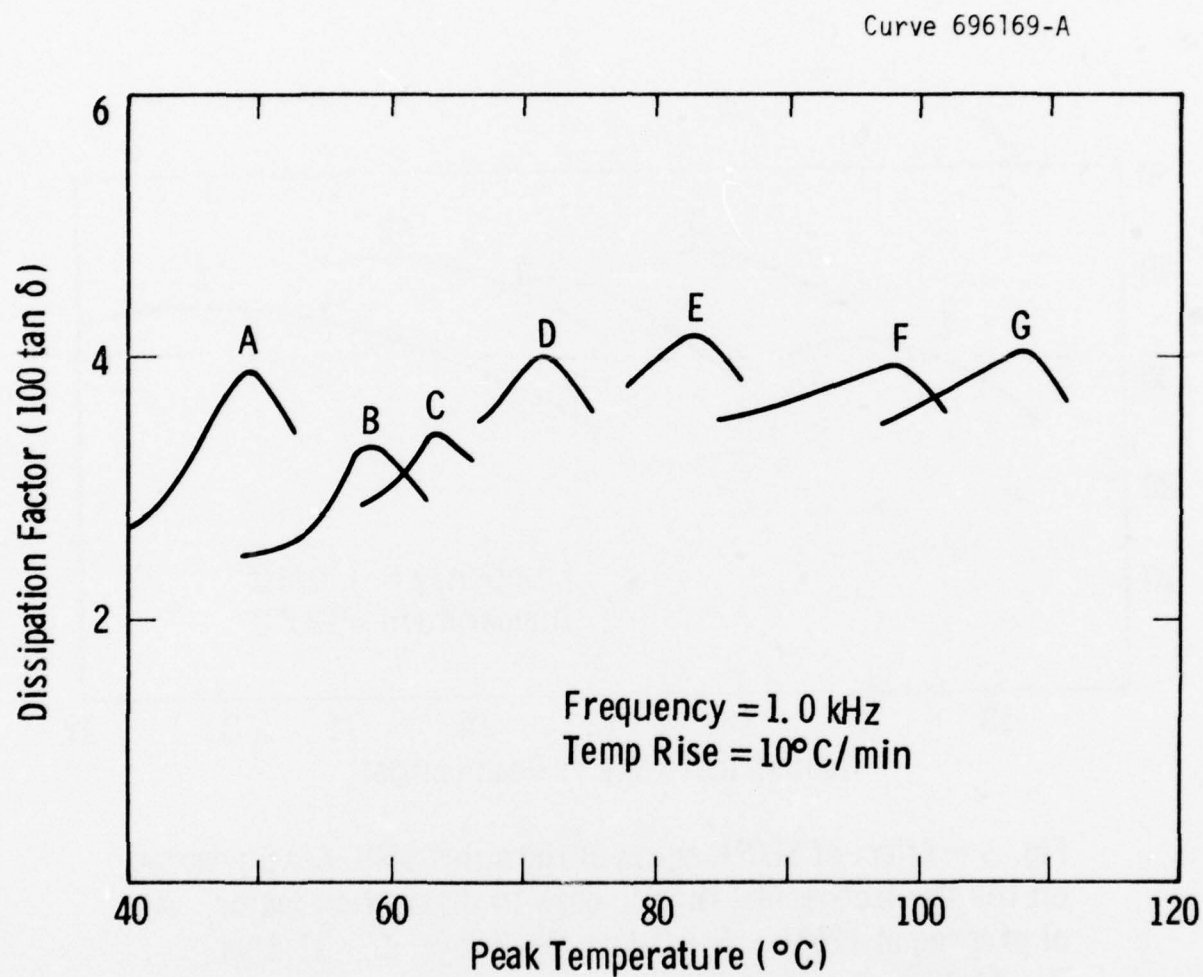


Fig. 4 — Effect of 120°F aging of Hercules 3501-6/AS prepreg on the temperature of the peak in dissipation factor associated with the solid-liquid transition. Age of prepreg at 120°F : A - 0 day, B - 2 days, C - 4 days, D - 8 days, E - 12 days, F - 18 days, G - 25 days

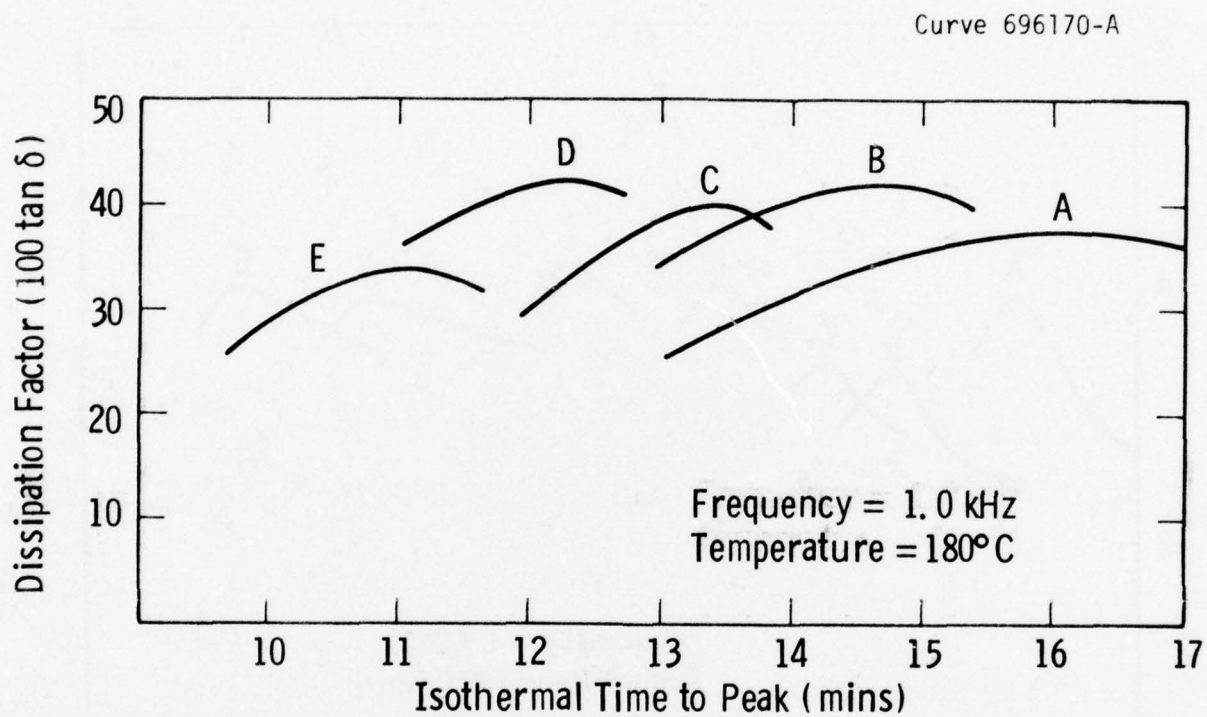


Fig. 5 - Effect of 120°F aging of Hercules 3501-6/AS prepreg on the the isothermal time to peak in dissipation factor. Age of prepreg at 120°F : A - 0 day, B - 8 days, C - 11 days, D - 14 days, E - 18 days

time with the age of the prepreg. This method is not as sensitive to small changes in the age of the prepreg as the first method described above.

### 3.3.1 Experimental Procedure

Table 3 lists the instruments used in this investigation with the model numbers and manufacturer. The principal instrument used is an automatic dielectrometer referred hereafter as Audrey. It is an automatic ac bridge with a frequency range of 0.1 to 1.0 kHz. Using a pair of electrodes on either side of the sample space, Audrey imposes a small voltage of selected frequency on the sample. The resulting current is measured and decoded to provide two sample responses - dissipation factor ( $\tan \delta$ ) and capacitance (C).  $\tan \delta$  can be measured from zero to infinity and C from 0-500 pF. The two responses are plotted along with the temperature of the sample as function of time on a 3-channel scanning recorder. An X-Y recorder is used to plot  $\tan \delta$  and C as a function of temperature. Both recorders can be operated simultaneously. Figure 6 shows a photograph of the instruments.

TABLE 3  
LIST OF DIELECTRIC ANALYSIS INSTRUMENTS USED

<u>Item</u>	<u>Instrument</u>	<u>Supplier</u>
Dielectrometer	Audrey II Model 203	Tetrahedron Assoc.
Scanning Recorder	SR-300, 3-Channel Recorder	Tetrahedron Assoc.
X-Y Recorder	Omnigraphic 2000 With Type 6 and Type 15 Modules	Houston Instruments
Heated Press and Test Cell	Di/An 300	Tetrahedron Assoc.
Temperature Controller for Test Cell	ATC-200	Tetrahedron Assoc.

For all experimental work requiring close temperature and pressure control, a dielectric analysis test cell (containing the sample) and a press called Di/An 300 is used. The press is electrically heated and has a maximum temperature of up to 370°C. It is located at the right of Figure 6. The



Fig. 6 - Instruments used for dielectric analysis.

press temperature is controlled by an automatic temperature controller. The sample is sized to fit inside a 2" aluminum weighing dish which also serves as the bottom electrode. The sample is covered by a 0.001" polyimide film as discussed in 3.3.2. The top electrode is usually a 1" diameter aluminum foil and is placed above the Kapton film. The sample temperature is measured by a thermocouple placed directly under the 2" aluminum dish. It is prevented from contacting the dish by a disc of 0.001" polyimide film.

Two procedures may be used to measure the degree of B-stage of the resin: either isothermal or temperature variant mode.

In the isothermal case, a convenient reaction temperature is selected; usually the final cure temperature for the resin (180°C). The empty test cell is preheated in Di/An 300. The sample is cut to size (usually 1 1/2" square or 1 1/2" in diameter) inside a 2" aluminum weighing dish. The press is opened and the dish is rapidly inserted within the test cell. Sufficient pressure is used to provide good contact without squeezing out too much resin. By carrying out the procedure quickly, isothermal conditions can be achieved within 1 minute.

In the temperature variant mode of observation, the sample and electrode assembly is the same, but the sample is placed in the test cell and press at room temperature. The press is then heated at a constant rate of 10°C/minute and the X-Y recorder is used to plot  $\tan \delta$  and C as a function of temperature.

### 3.3.2 Sample Geometry

Since the graphite is conductive, if the electrodes are directly placed on the sample, a response which does not vary with time or temperature is found. One of the electrodes was separated from the sample prepreg by a 0.001" thick non-conductive polyimide film (Kapton<sup>®</sup>). In any case, it is advantageous to use such a barrier between the sample and one of the electrodes.<sup>(2)</sup> With graphite the magnitude of the peaks are quite small, e.g., Figure 4 shows the magnitude of the peaks to be between 3% and 4%. The peak magnitudes can be enhanced by inserting 1 ply of glass fabric between the sample and the polyimide film. When this is done, the glass-polymer

region becomes the sample space. The larger magnitude of the peaks is shown in Figure 7. The magnitude of the peaks is about 28% as opposed to 4% without the glass. Heat cleaned style 181 glass fabric was used.

We would have preferred to use the glass fabric in all our DA studies but in measuring the temperature of the relaxation peak associated with the softening and flow of the resin, this sample geometry produced a far greater degree of scatter than the results without the fabric. This presumably because the resin has to flow into the fabric and with age, the flow becomes somewhat erratic. With the isothermal mode of operation, this was found not to be a problem because the temperature is high enough to allow the cloth to be saturated rapidly.

Thus, all the DA isothermal time to peak results reported herein used a sample geometry which consisted of 2 ply of prepreg, 1 ply of heat cleaned 181 style glass, and 1 ply of 0.001" polyimide film.

All of the DA results giving the temperature of the peak in dissipation factor used a sample geometry which consisted of 1 ply of prepreg and 1 ply of 0.001" polyimide film.

### 3.3.3 Effect of Humidity

During the experiments on high humidity aging of the prepreg, we noted that the temperature of the peak in dissipation factor was much lower (8-10°C differences were noted) than expected and also the results were erratic. This was caused by the saturation of the prepreg with water. To overcome this problem, the samples had to be conditioned in a dry dessicator for a minimum of 2 hours prior to test. This was sufficient to bring the results up to within 1-2°C of a totally dry sample. DA measurements made in a laboratory environment having high humidity would require similar treatment.

## 3.4 DYNAMIC MECHANICAL ANALYSIS (DMA)

The various forms of dynamic mechanical analyses can be considered to be analogous to dielectric analysis except that the stresses applied are mechanical instead of electrical. This similarity has been shown for one epoxy resin system<sup>(2)</sup> where dielectric analysis results were compared to published Torsion Braid Analysis (TBA) results.

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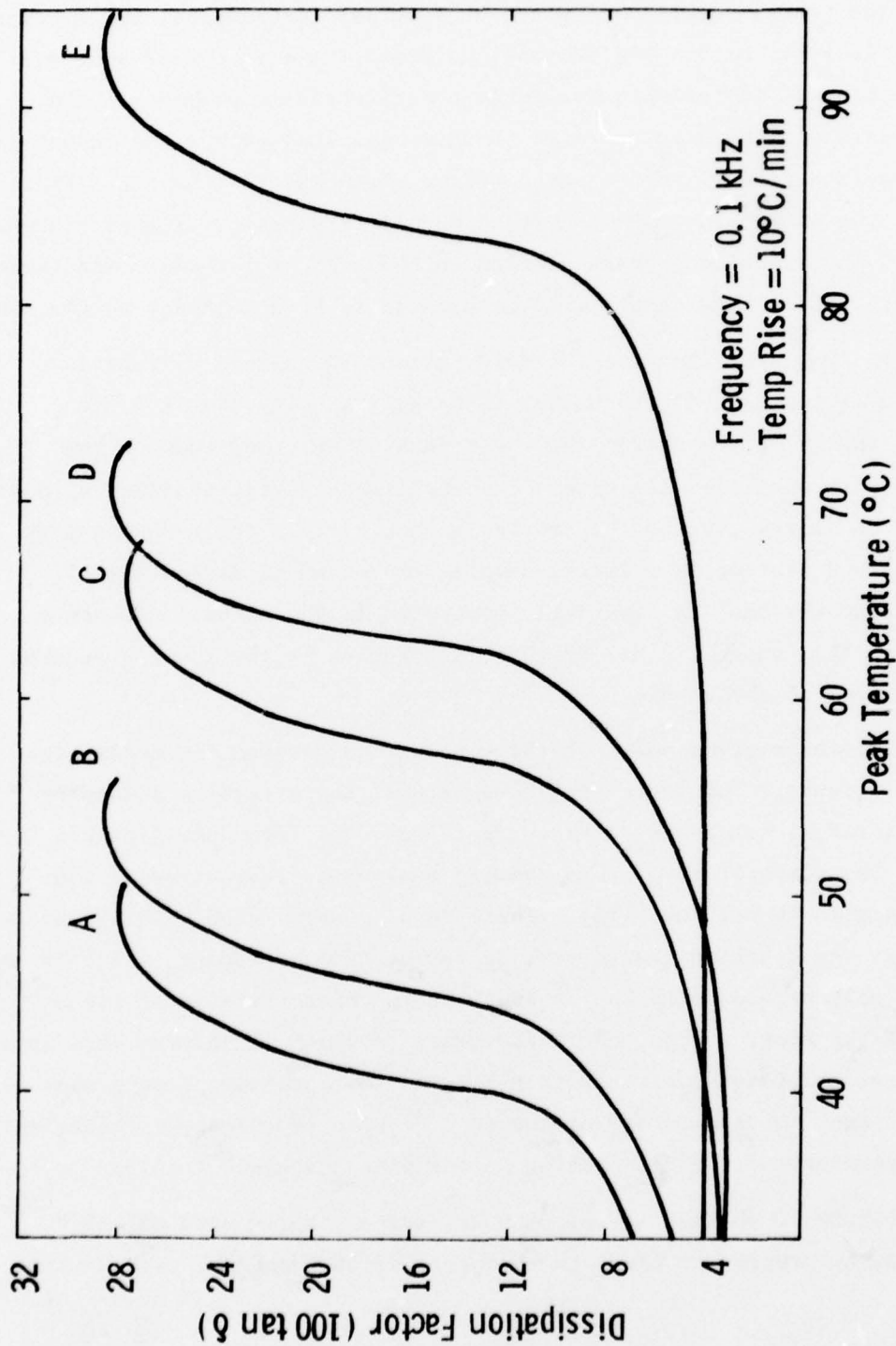


Fig. 7 - Effect of 120°F aging of Hercules 3501-6/AS prepreg on the temperature of the peak in dissipation factor associated with the solid-liquid transition [using 1 ply of glass fabric as part of the sample] A - 0 Day, B - 2 Day, C - 8 Day, D - 10 Day, E - 14 Day

The instrumentation consists of a DuPont Instruments, 980 Dynamic Mechanical Analyzer with a 990 Thermal Analyzer. This is one of several dynamic mechanical instruments available to characterize polymers. DMA in this report will be used to refer to this apparatus only. The DuPont DMA does not operate at a fixed frequency, unlike the other instruments. Figure 8 shows a photograph of the DMA with its controller/recorder. Figure 9 shows a sample of the graphite prepreg clamped in the arms of the DMA. The thermocouple which records the sample temperature can be seen adjacent to the sample.

In DMA, after the initial deformation, the sample is kept in oscillation at its natural frequency. Damping gradually converts the mechanical energy of the system into heat causing the amplitude of the oscillations to decrease with time. The amplitude is kept constant by adding the amount of energy lost by the sample in each cycle. The makeup energy is measured and plotted as relative damping expressed in decibels (dB). A second parameter that is constantly monitored is the natural resonance frequency of the sample (in Hz) which is a function of the Young's modulus (the stiffness) of the sample.

If, for a given polymer, the damping and natural frequency are plotted as a function of increasing temperature, there results a damping peak associated with a rapid decrease in the natural frequency (Young's modulus). The temperature of this damping maximum is indicative of the glass transition temperature ( $T_g$ ). There is a  $T_g$  associated with all states of cure. As the reaction progresses,  $T_g$  increases. A prepreg, which is only marginally polymerized, also has an apparent  $T_g$  characteristic of its B-staging or age. As the prepreg ages, the temperature at which it softens (its apparent  $T_g$ ) increases. This property can then be used to track the prepreg age. The shift, with age, in temperature of the damping peak is analogous to the shift in the temperature of the dissipation factor peak discussed in 3.3.

Figure 10 shows a series of peaks for a prepreg aged at 120°F, 95% RH. As the prepreg is aged, the temperature at which the peak occurs increases.

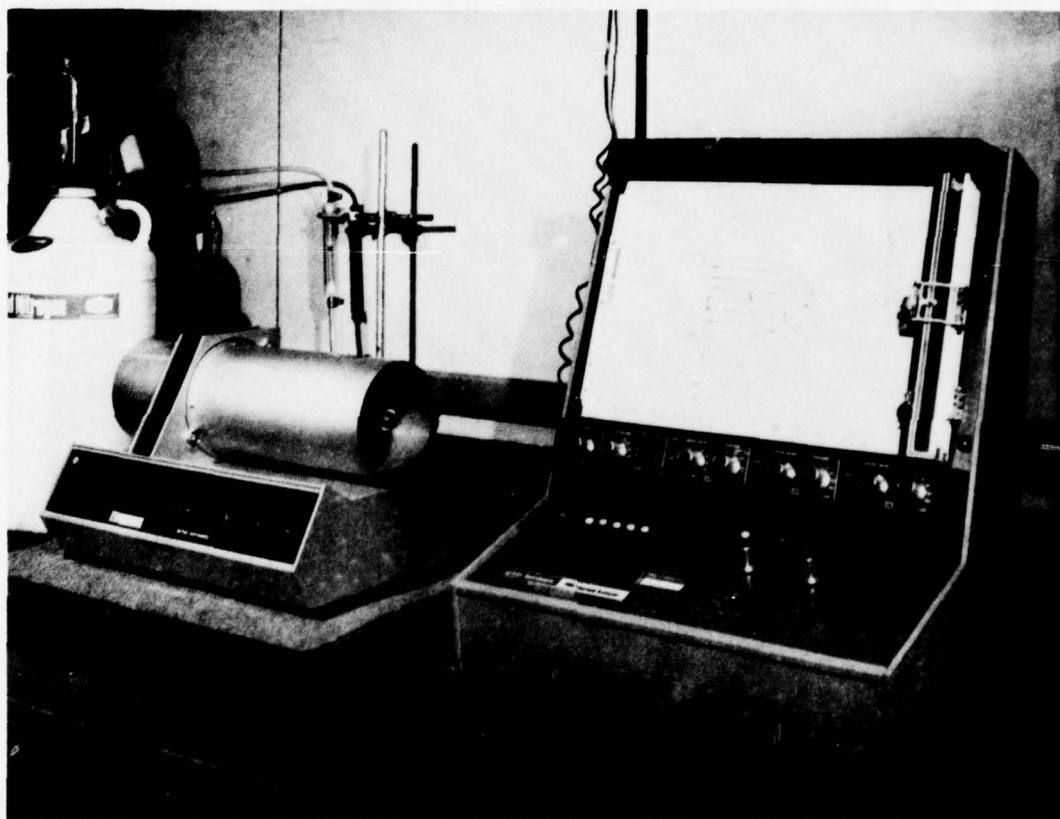


Fig. 8 - The DMA instruments.

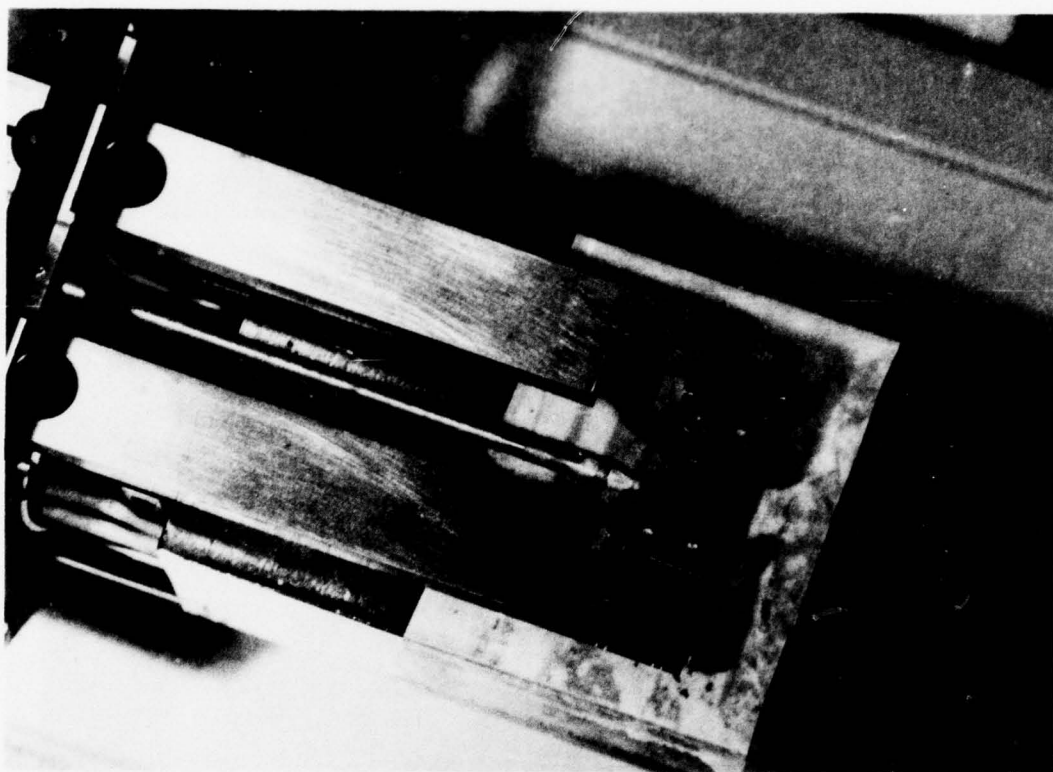


Fig. 9 - Sample of graphite prepreg clamped in the DMA oscillating arms.

Curve 696172-A

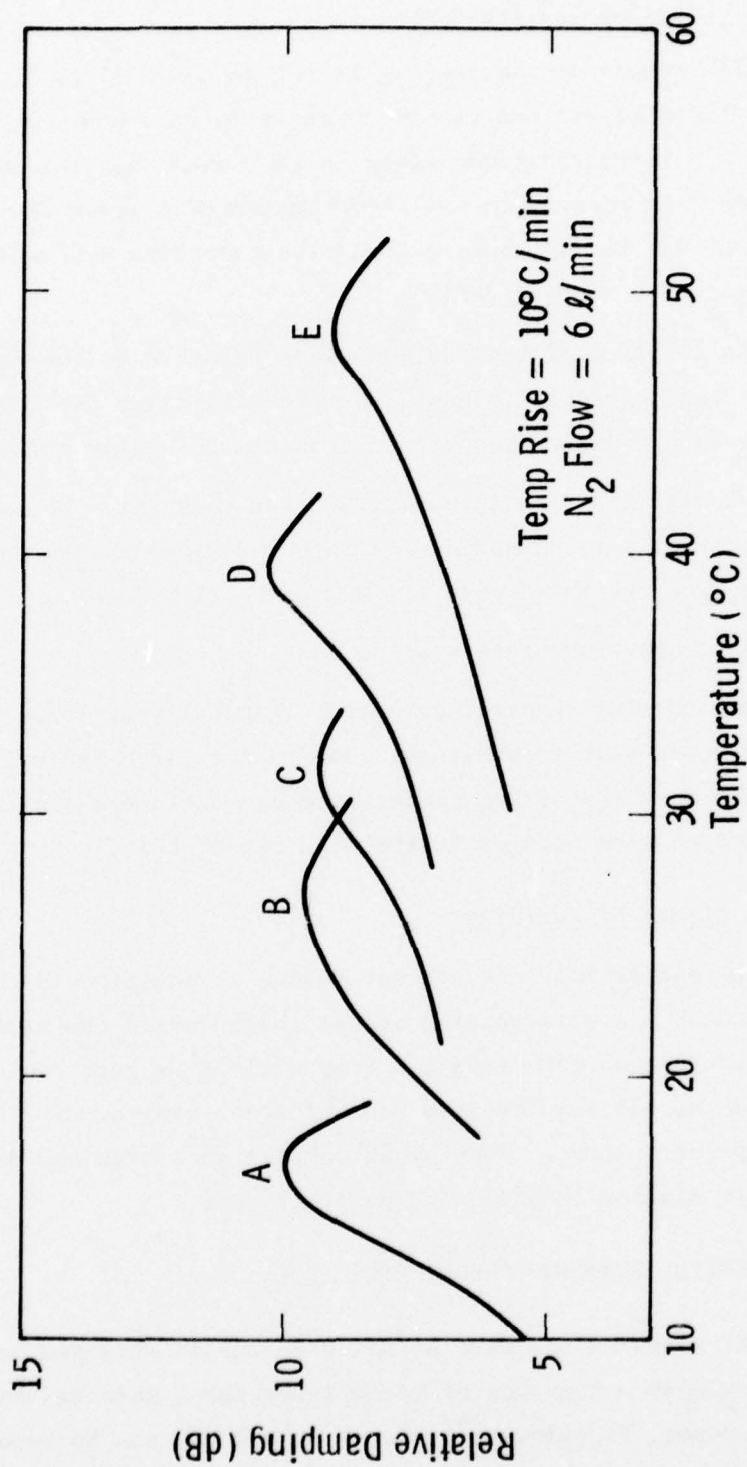


Fig. 10—Effect of aging (120°F, 95% RH) of Hercules 3501-6/AS prepreg on the temperature of the peak in relative damping (DMA). Aging time: A - 0 day, B - 1 days, C - 2 days, D - 3 days, E - 4 days

#### 3.4.1 Experimental Procedure

The sample of the prepreg is cut to about 1" by 1/2" and then clamped horizontally in the clamps as shown in Figure 9. In general, the manufacturer's recommendations given in the manual are followed. Initially (the equipment is relatively new) we experienced a great deal of scatter in the data from day to day, but we found the following precautions allowed us to obtain good low scatter data: -

1. The location of the thermocouples relative to the sample must be kept constant. This is particularly true for the thermocouple reading "sample temperature", as it can easily shift.
2. The nitrogen flow rate must be kept constant. We used the manufacturer's recommended 6 l/min. The plumbing has to be periodically checked for leaks down stream of the flow meter.
3. The temperature rate must be constant.
4. The starting temperature must be generally at least 40°C below the expected peak temperature. Due to the large thermal mass of the system, the starting temperature can influence its thermal dynamics thus causing changes in the peak temperature.

#### 3.4.2 Effect of Humidity

High sample moisture content causes a reduction in the temperature of the damping peak - a plasticizing effect which lowers the apparent Tg of the sample. Depending on conditions, a drop of 10°C or more can be experienced. For this reason, all samples were conditioned a minimum of 2 hours in a dry desiccator prior to test. Testing of samples in a high humidity environment would require similar conditioning prior to test.

### 3.5 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC measures the rate at which energy is released or absorbed from the sample as a function of temperature for a selected heating rate. In a recent paper, Pappalardo<sup>(4)</sup> has shown how DSC can be used to measure the relative age of the prepreg, by measuring the heat of residual cure of

the sample. This has also been shown by Hagnauer, et al.<sup>(5)</sup> for one aging condition for an epoxy resin mix. Carpenter<sup>(6)</sup> has shown that the temperature of the peak isotherm decreases with age of the prepreg.

As a prepreg or resin ages, some of the reaction takes place during the aging process. Therefore, the total exotherm or heat of residual reaction should decrease. Also since the DSC measures at some linear temperature increase rate, the diminishing exotherm should result in a lowered peak temperature.

Figure 11 shows a typical DSC scan using the DuPont 900 Thermal Analyzer. As recommended by the manufacturer, the sample is put in the reference pan, thus the exotherm is recorded as an endotherm. The peak temperature of exotherm for this scan is 232°C. There is also a minor exotherm at about 160°C. All samples were run at a rate of 10°C/min.<sup>(4)</sup> The heat of residual cure is measured from the area under the curve. The area under the curve can be the total area as bounded by the solid line or the "A" type areas as bounded by the dotted line (see Figure 11). The former was used as it gave better results. Tin, indium, and zinc standards were used to calibrate the cell and obtain the "E" value as recommended in the manual.

### 3.6 CHEMICAL METHODS

The chemical analysis during the aging of the prepreg was very kindly performed by Dr. G. L. Hagnauer of the Polymer and Chemistry Division of the Army Materials and Mechanics Research Center. His data is presented here in brief with his permission.

A sample of prepreg which had been stored in the freezer for about 90 days was shipped in dry ice to AMMRC and tested there during exposure to ambient conditions ( $72 \pm 1^\circ\text{F}$ ) for 53 days. At intervals, multiple samplings of the prepreg were made. The methods used are explained in detail in Reference 5.

By preparative LC (liquid chromatography) and FTIR (Fourier transform infrared), significant reductions were found in the level of the curing agent (DDS) and tetraglycidyl methylene dianiline (TGMDA) which is the main component of the principal epoxide in the resin mix. A major reaction product of the

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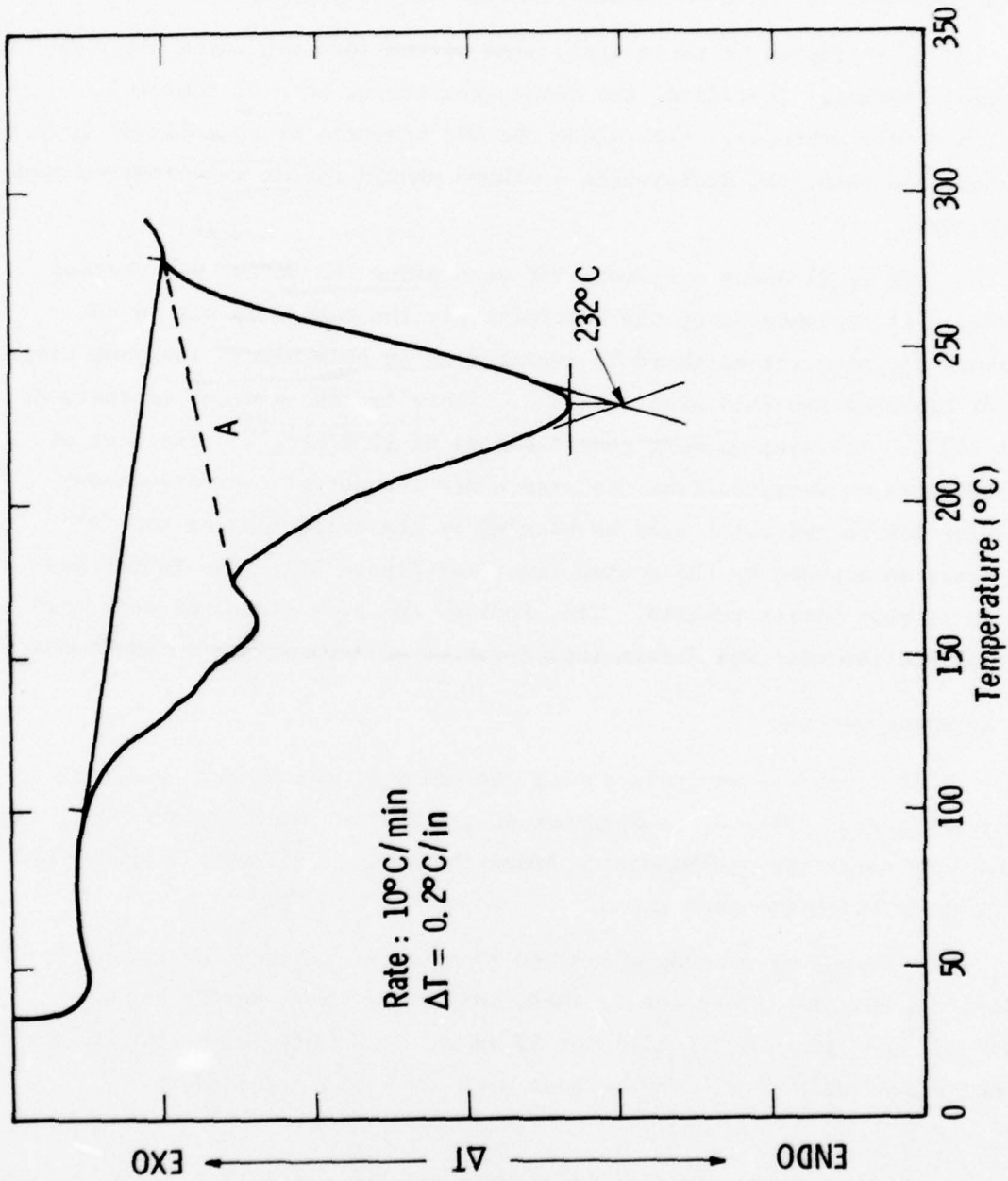


Fig. 11 - Typical DSC scan of Hercules 3501-6/AS prepreg. This scan is for unaged prepreg

two was also identified and was found to increase with time. Figure 12 shows a plot of these changes as a function of age. If the original amounts of TGMDA and DDS present are known, the age of the prepreg can be successfully followed using chemical methods. Alternatively, the age of the prepreg can be followed by measuring the amount of the "product" present in the prepreg. However, its amount does not change as rapidly as the amounts of TGMDA and DDS presumably because of the formation of many other products.

### 3.7 PREPREG PHYSICAL PROPERTIES

The physical properties of the prepreg measured during the aging studies were tack and resin flow.

#### 3.7.1 Prepreg Tack

Prepreg tack is its ability to adhere to a substrate or to itself. No good tack test is available because to an extent, the property is subjective and depends on the end use. Pieces of prepreg being laid flat would require minimal tack; complex shapes and vertical layup would require a great deal of tack. A prepreg is tacky when at the ambient or use temperature the resin system is above its glass transition temperature ( $T_g$ ). Then, when some reactions take place during storage or aging, increasingly larger molecular weight species are formed and the  $T_g$  of the prepreg increases above the ambient or use condition and the prepreg then loses its tack. Thus tack is influenced by: (1)  $T_g$  of the prepreg, (2) ambient temperature - increasing ambient temperature will increase tack, (3) humidity - increasing humidity will increase tack if the resin picks up any moisture, (4) resin content, and (5) test parameters.

Since the prepreg was supplied by Hercules, their test procedure was used to measure the tack of the prepreg. It is a go/no go test with the prepreg either passing or failing. The test is specified in Hercules, Inc. Graphite Composite Testing Procedures HD-SG-2-6006C, Section 5.4. Since the tack is the critical property of this prepreg, the test procedure is reproduced in Appendix B. The tack test was performed at ambient conditions.

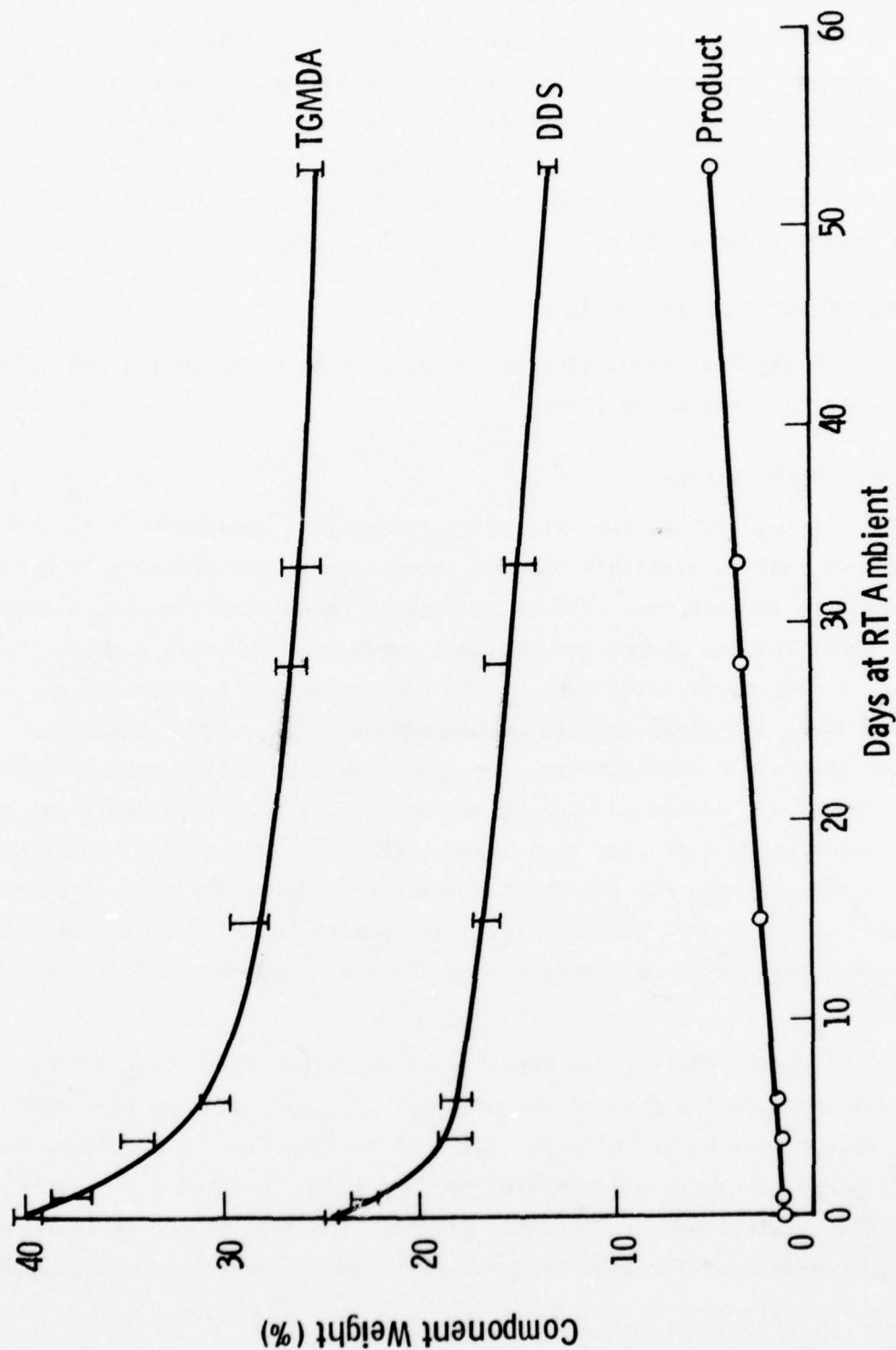


Fig. 12 - Changes in chemical composition of resin during RT aging of Hercules 3501-6/AS prepreg (Data of Dr. G. Hagnauer, Army Materials and Mechanics Res. Center)

### 3.7.2 Resin Flow

Resin flow was determined by a press laminating procedure as detailed in Hercules Testing Procedures HD-SG-2-6006C, Section 5.3.1. It is also reproduced in Appendix B. (Note: Two tests were performed for resin flow and prepreg tack for each sample as called for in the test procedures.)

### 3.8 LAMINATE PROPERTIES

We were interested in determining the changes taking place in selected laminate properties, as the prepreg was aged. Thus, no attempt was made to obtain optimum properties or to modify the cure cycle with age.

Unidirectional laminates were press molded in a matched-metal mold which gave a laminate thickness of approximately 0.080". The mold was prepared as detailed in Hercules Test Procedure HD-SG-2-6005C, Section 5.1.1. Sixteen plies of prepreg were used to yield a cured nominal ply thickness of 0.005". The cure schedule used was similar to the autoclave cure schedule given in the Hercules Data Book for 3501-6/AS prepreg. The cure schedule used is as follows:

1. Insert mold and prepreg into cold press and apply contact pressure.
2. Heat press at a rate of 20°F every 10 mins to 360°F + 5°F.
3. Apply  $85 \pm 5$  psi when the temperature reaches 250°F.
4. Hold at 360°F for 120 + 15, -0 mins.
5. Cool to less than 150°F over 1 hr period before removing mold from press.

Due to an oversight, some of the initial laminates were tested without a post cure. When this was discovered, some laminates were post cured 8 hrs at 180°C and the results were compared to similarly aged non-post cured samples. No real differences in the measured mechanical properties were found and, therefore, to preserve consistency with previous results, no postcure was used.

The laminate test specimens were cut from the panel and tested according to Hercules, Inc. Test Procedure HD-SG-2-6002C. Cutting was done according to Section 5. Resin contents were obtained according to Section 6.2.2 (for A type fiber). Flexural strength and modulus was measured at room temperature according to Section 7.1, and the short beam shear strength at room temperature according to Section 7.3.

#### 4. AGING STUDIES WITH 3501-6/AS PREPREG

The data from the aging studies is presented in graphical form. The error bars on the data points represent  $\pm 1$  standard deviation. Lines where shown are linear regression. The data for the TTW does not have error bars because the readings were usually within 1/2 unit of each other and the reading accuracy is not much better than that in the present package configuration (see Figure 1). Since all the measurement methods have been discussed in Chapter 3, no details of specific measurements will be discussed here.

##### 4.1 USEFUL LIFE OF THE PREPREG

It was found during our series of aging studies that the prepreg (3501-6/AS) lost its tack and its drapability before any other property deteriorated. This was confirmed by the supplier. Prepreg tack became the critical property for this prepreg as it is the first property to deteriorate with age. Thus, for the purposes of this study, the useful life of the prepreg was considered over when it had lost its tack. All the results of the age indicating tests were correlated to the loss of tack under various aging conditions. The tack was not measured at the aging condition, but under ambient conditions (see 3.7.1).

##### 4.2 120°F DRY AGING

This series was carried out to well beyond the useful life of the prepreg, and data for this aging condition is presented in Figures 13-18. Figure 13 presents the dielectric analysis (DA) and the TTW data. It shows that the prepreg loses its useful life in about 2 days at this condition at which point the TTW reading is about 6 and 1 kHz dissipation factor peak temperature is 60°C. The DA data shows a good trend of increasing peak temperatures with age. Figure 14 presents isothermal time to peak data obtained by DA. The trend with age is not as strong and initially there is no perceptible change. After 5 days the 1.0 kHz peak time diminishes quite rapidly.

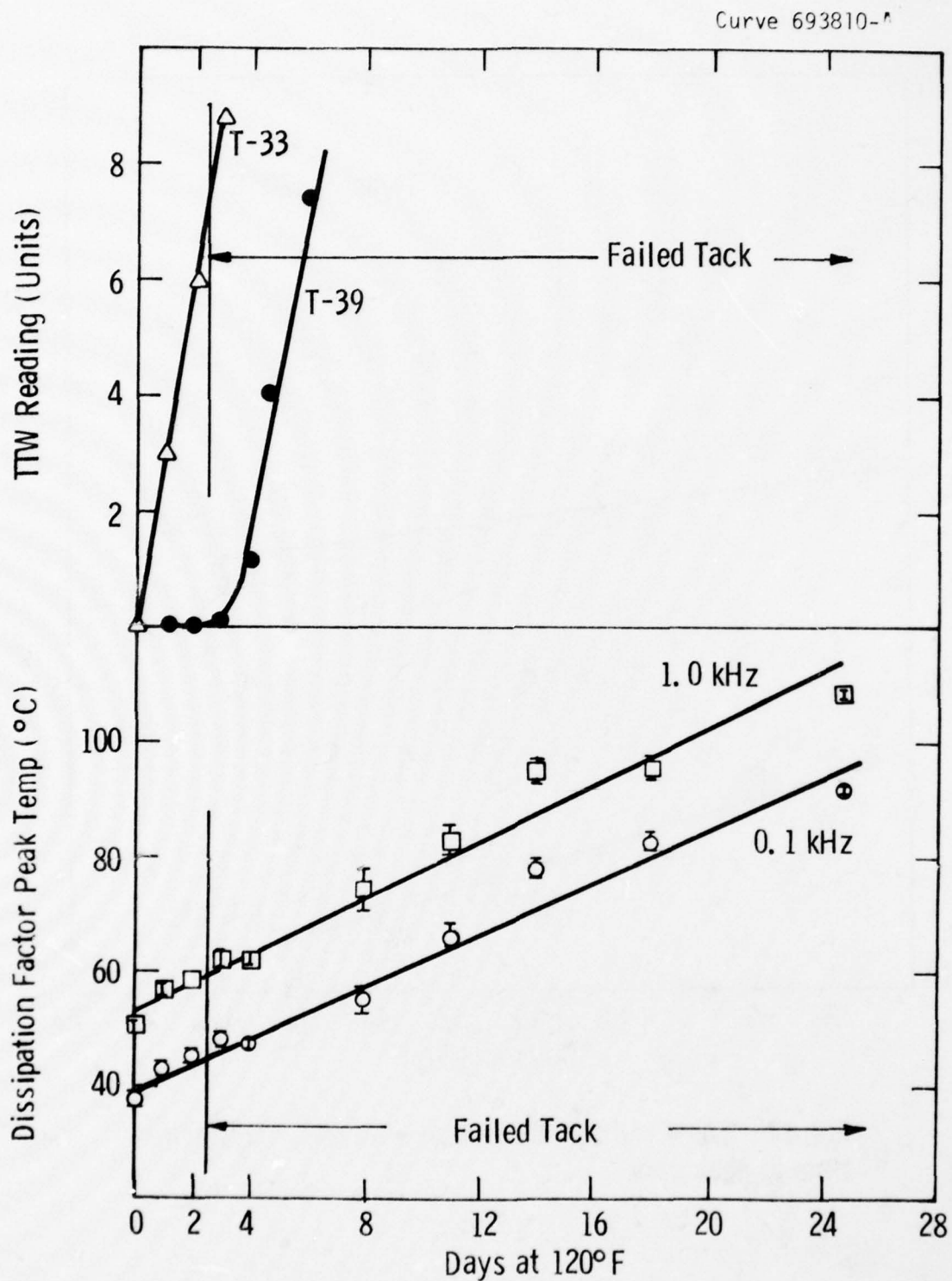


Fig. 13- 120°F Aging - dielectric analysis & TTW data

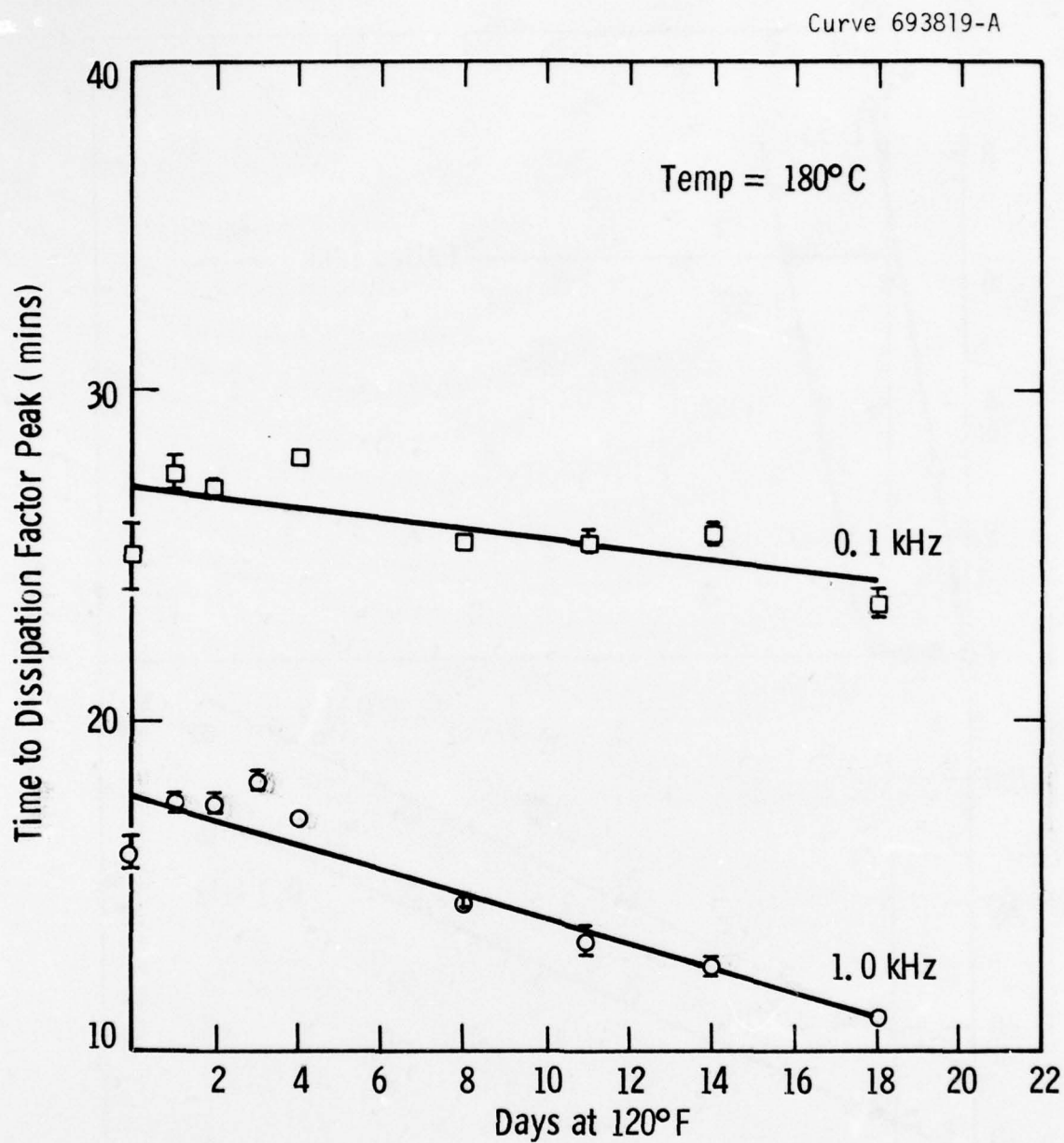


Fig. 14- 120°F aging - dielectric analysis, isothermal time to peak data

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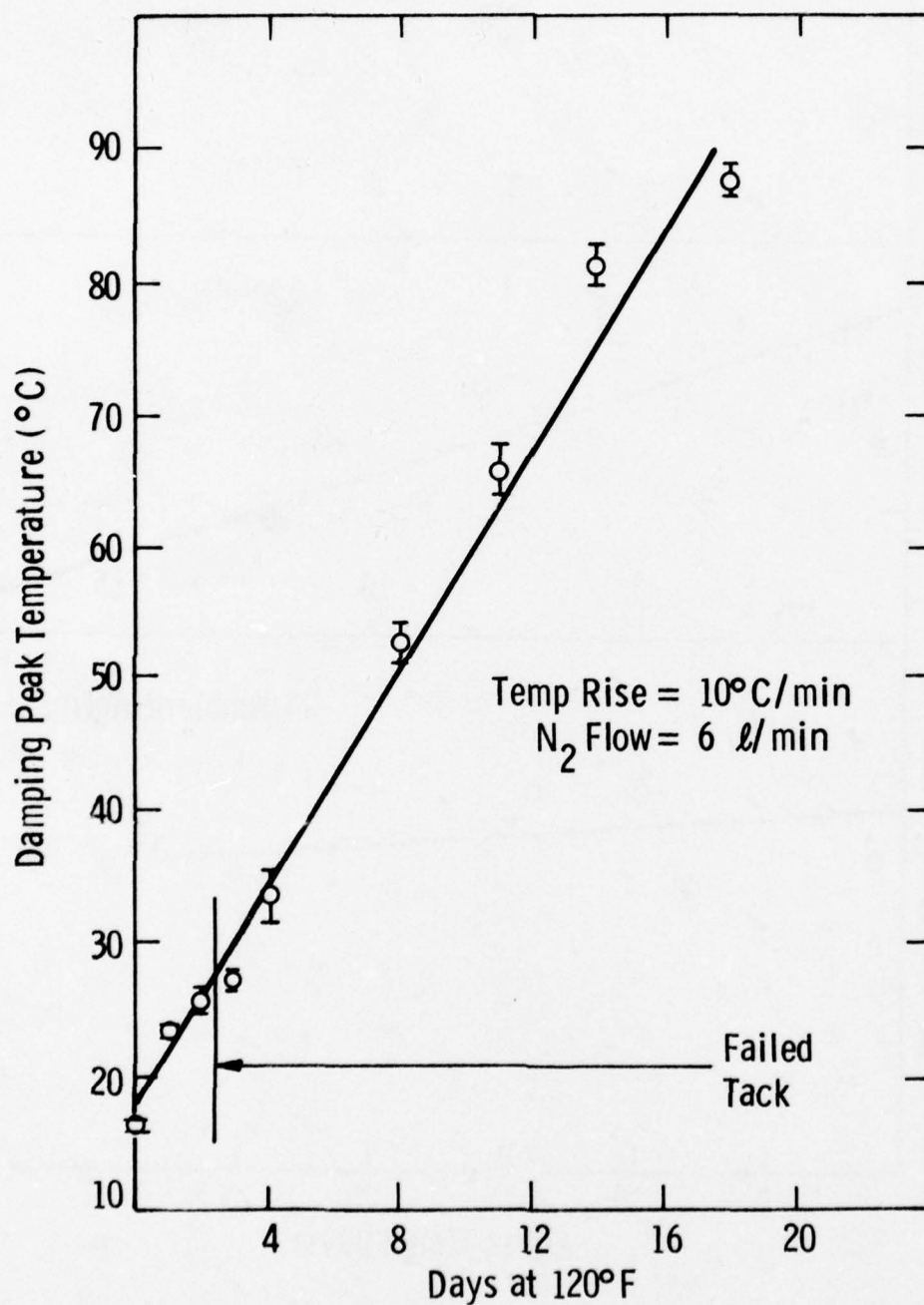


Fig. 15 - 120°F aging - DMA data

Curve 693812-A

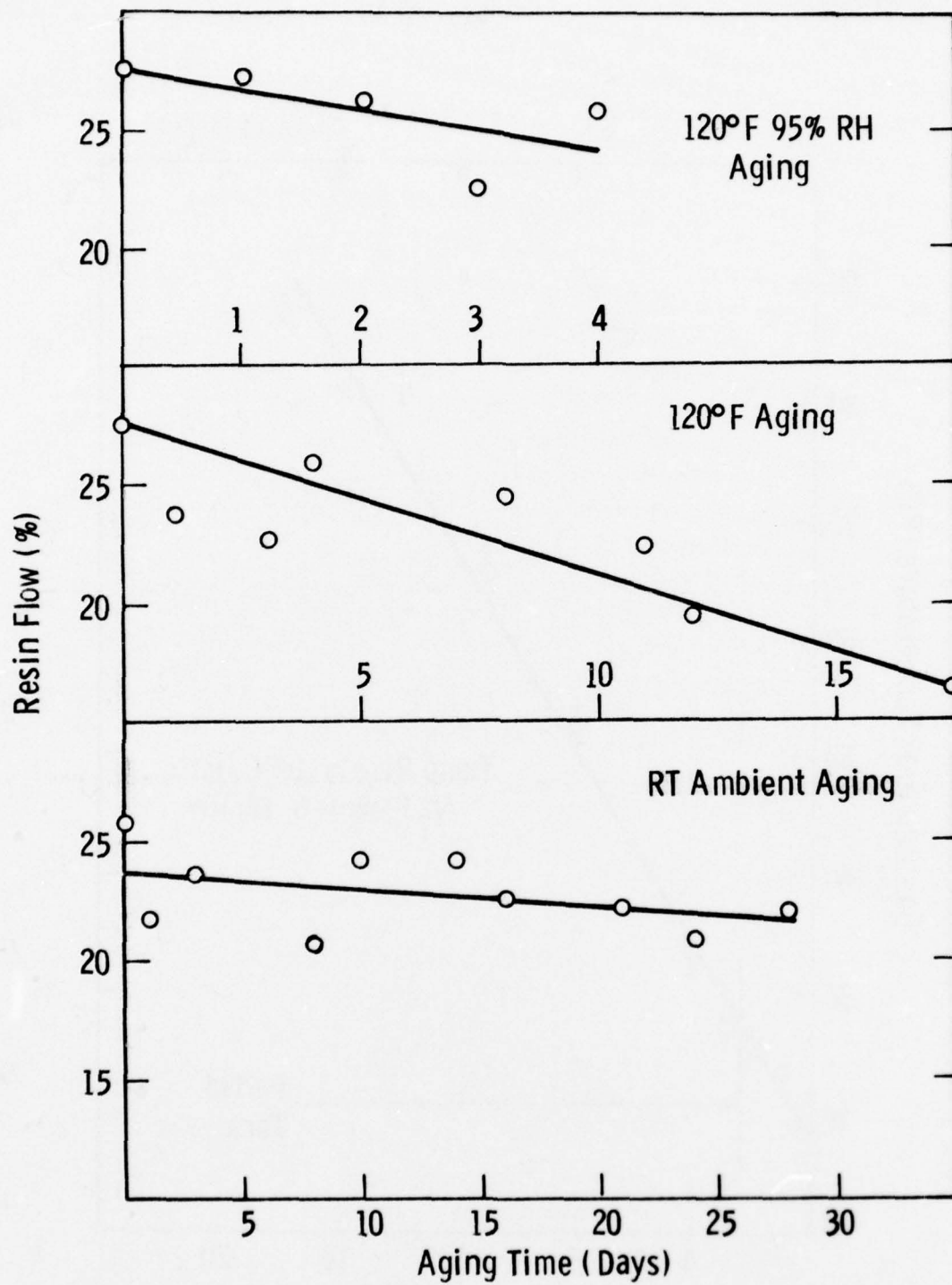


Fig. 16— % Resin flow as a function of aging

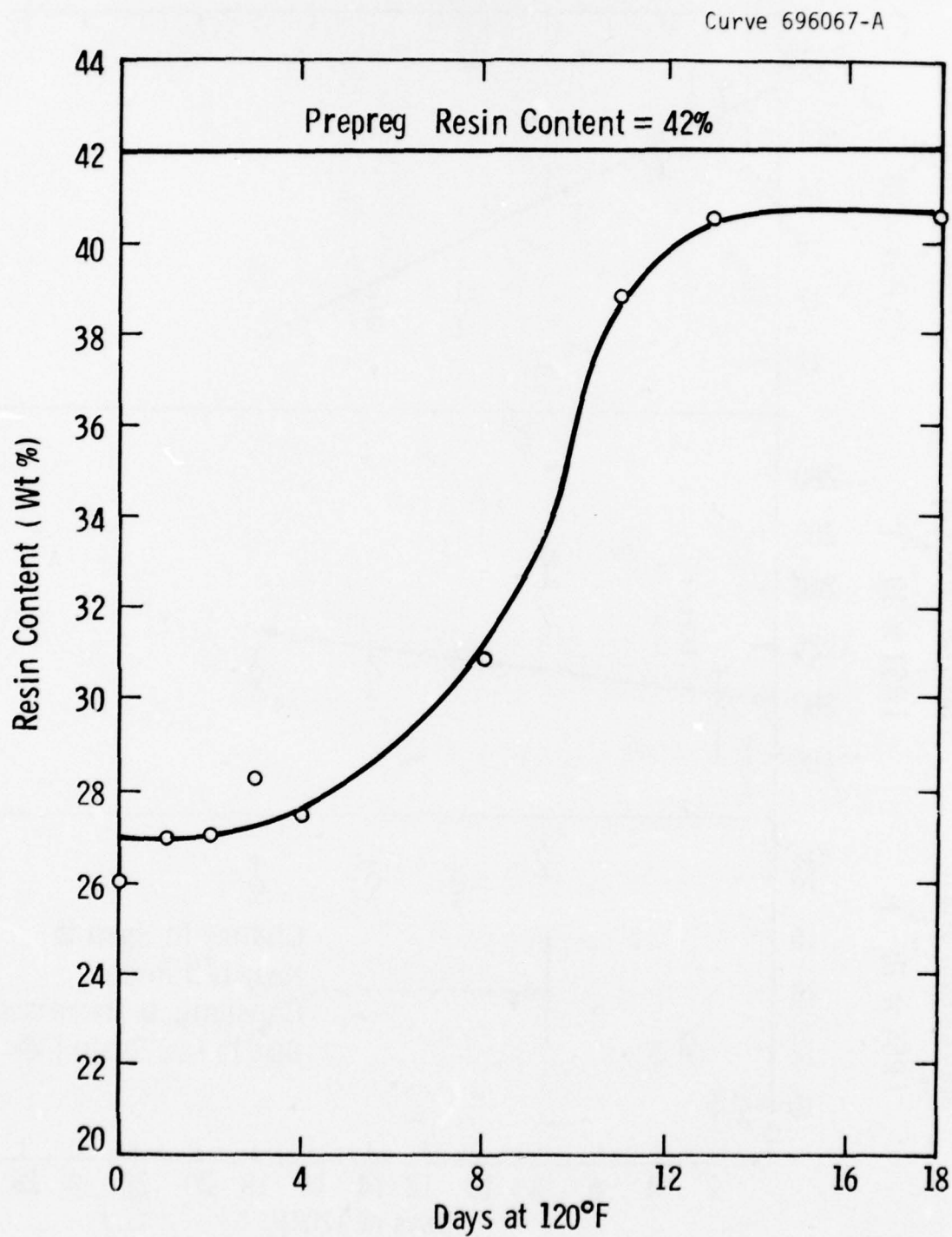


Fig. 17 - Resin content of laminates made from prepreg aged at 120°F

Curve 693815-A

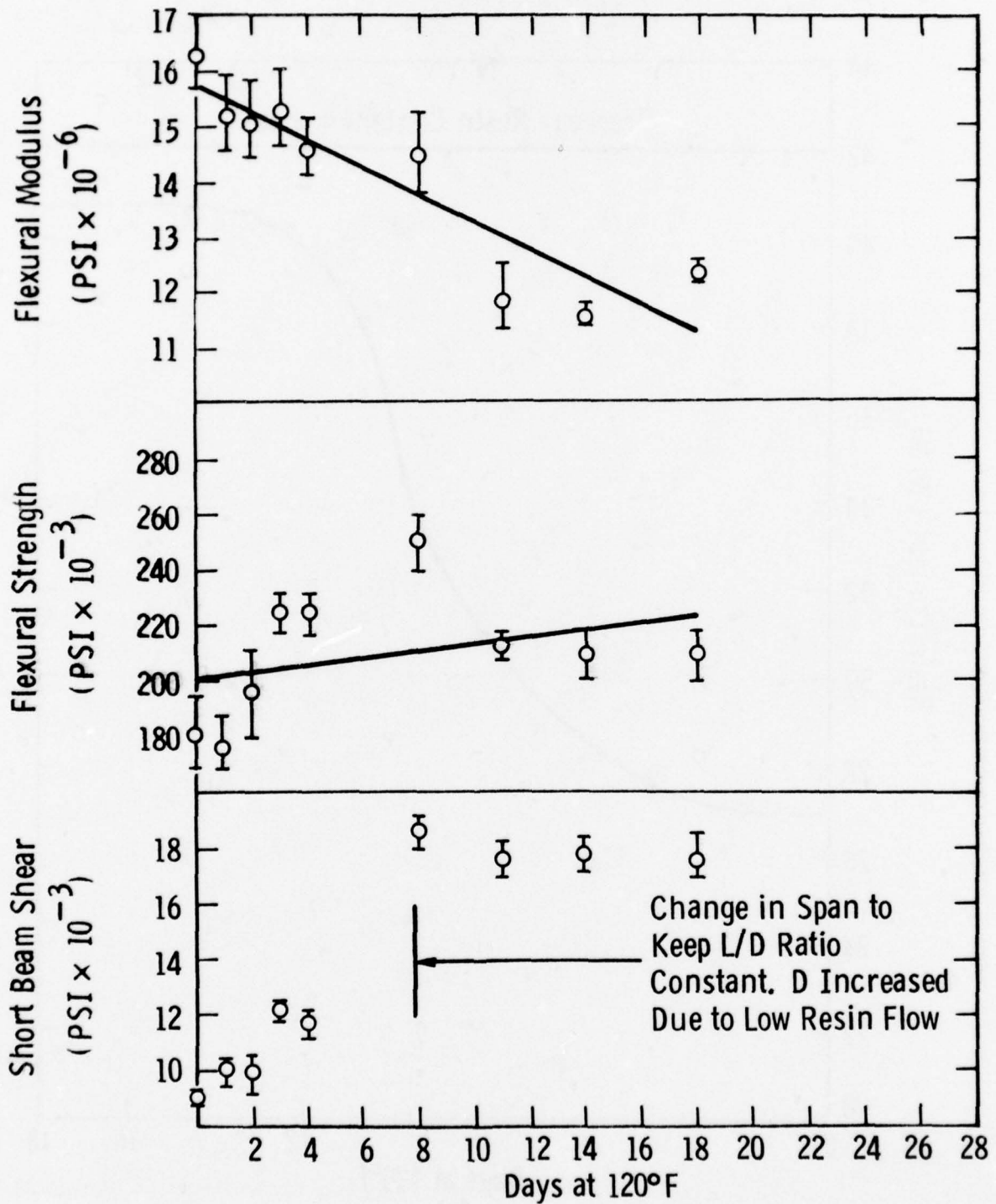


Fig. 18— 120°F aging - mechanical test data

Figure 15 presents the DMA data which correlates well with the age of the prepreg. The temperature of the relative damping peak increases quite rapidly with age. The prepreg lost its tack when the damping peak temperature was about 27°C. This is lower than the value found in the other aging experiments described later. Chronologically, this series was done first and we were cooling the apparatus only 10-20°C below the expected peak temperature (see 3.4.1). Therefore, this resulted in somewhat lower peak temperatures.

Figure 16 (center) shows that as the prepreg is aged, resin flow gradually diminishes. No real change occurs until after 8 days, but note that by this time the prepreg is well past its useful life at this aging condition (120°F). Figure 17 shows that as the prepreg is aged, the resin content of laminates made from it increases. This is because the resin flow (Figure 16) is diminishing with age. The net effect can be seen in the mechanical properties shown in Figure 18. Initially due to excessive squeeze out of the resin, the flexural strength and shear strength are low. As the resin content increases, the modulus (which depends on the fiber content) decreases slightly, but the flexural strength and shear strength increase. After 8 days of aging, as resin content begins to rise sharply (see Figure 17), both the strength values diminish somewhat, and the modulus drops sharply.

Figures 16, 17 and 18 together show that, depending on the age of the prepreg, if a standard cure cycle is used, properties can vary quite substantially. The data also shows that the material can provide good mechanical properties substantially beyond its useful life, if in the processing, tack is not important.

Table 4 presents the DSC data. We had expected very good results from the DSC method because the literature indicated it could be used to track the age of resins and prepreg. However, as Table 4 shows, the data is too scattered to be useful. There is some slight indication of decreasing peak temperatures between 3 and 8 days aging, but the trend does not continue. Similarly, the trend in decreasing  $\Delta H$  only occurs after 8 days, well past the useful life of the prepreg. The scatter in the data is probably due to the fact that we were examining the prepreg and minor local differences in

the resin/fiber weight ratio would seriously affect the results. We do not believe that there is sufficient reaction taking place during the aging periods considered to overcome the variability in the resin/fiber weight ratio.

TABLE 4  
120°F AGING - DSC DATA  
AVERAGES OF THREE RUNS

<u>Age at 120°F (Days)</u>	<u>Peak Exotherm Temp. (°C)</u>	<u>ΔH (Cals/gm)</u>
Fresh	233	31.5
1	236	30.0
2	233	25.9
3	235	30.6
4	230	28.0
8	227	29.8
11	235	16.9
13	235	13.0
18	247	28.9

#### 4.3 120°F, 95% RH AGING

Data is shown in Figures 19 to 22 and the results are similar to that for the 120°F dry aging. The TTW Type 33 is slowed down by the high humidity and has a reading of 4.5 after 2 days at 120°F, 95% RH, which again is the end of the useful life of the prepreg (Figure 19). DA results presented in Figure 19 show the expected increase in dissipation factor peak temperature with age and the correlation with loss of tack - about 60-62°C for the 1 kHz peak temperature. Figure 20 shows the DA isothermal time to peak data which, as expected for this short aging period, shows no real trend. All DA results are from samples conditioned a minimum of 2 hours in a dry desiccator.

Figure 21 presents the DMA data which shows the expected increasing damping peak temperature with age. Samples were placed in a dry desiccator for a minimum of 2 hours prior to test. Loss of tack occurs when the damping

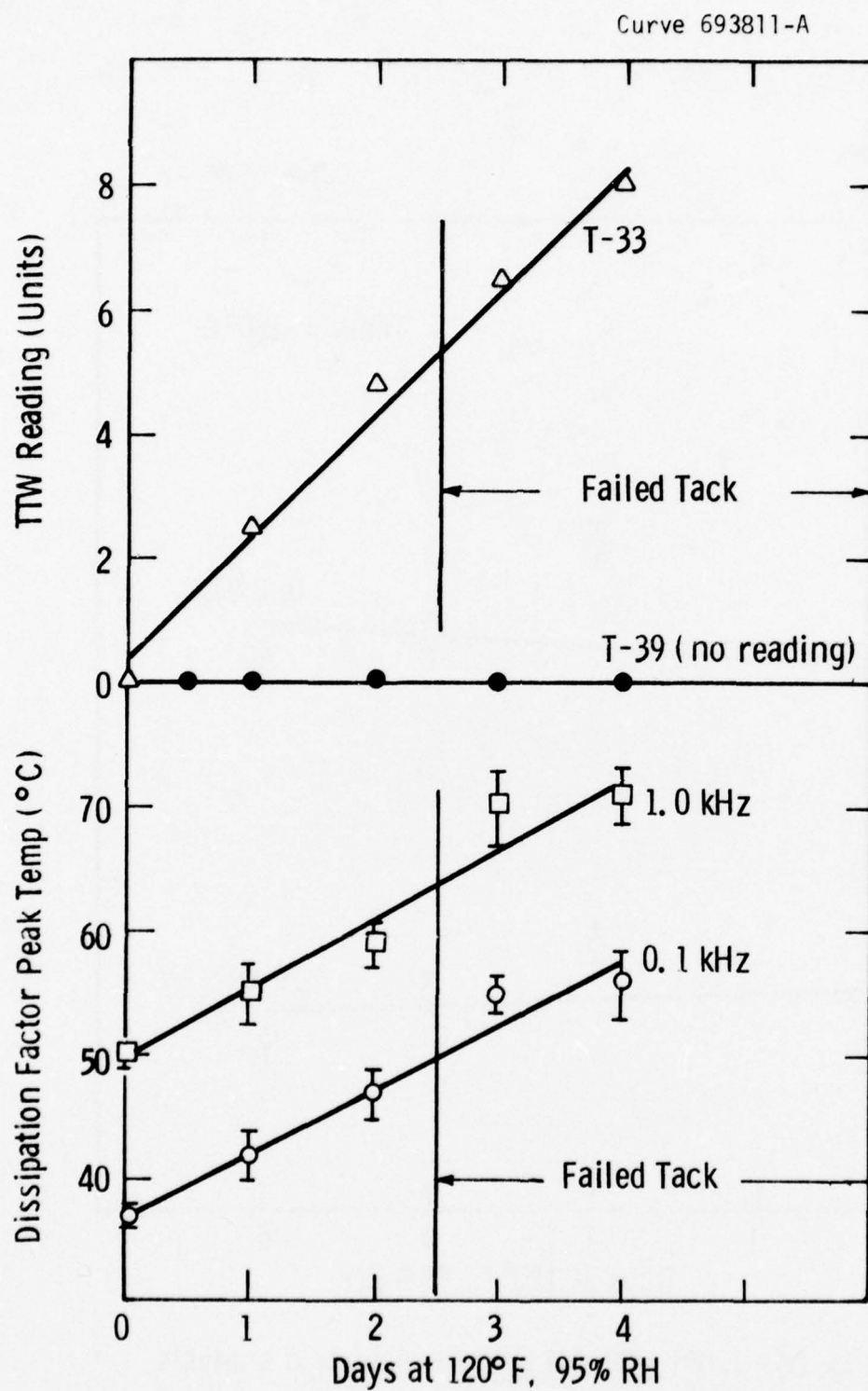


Fig. 19— 120°F, 95% RH aging - dielectric analysis and TTW data

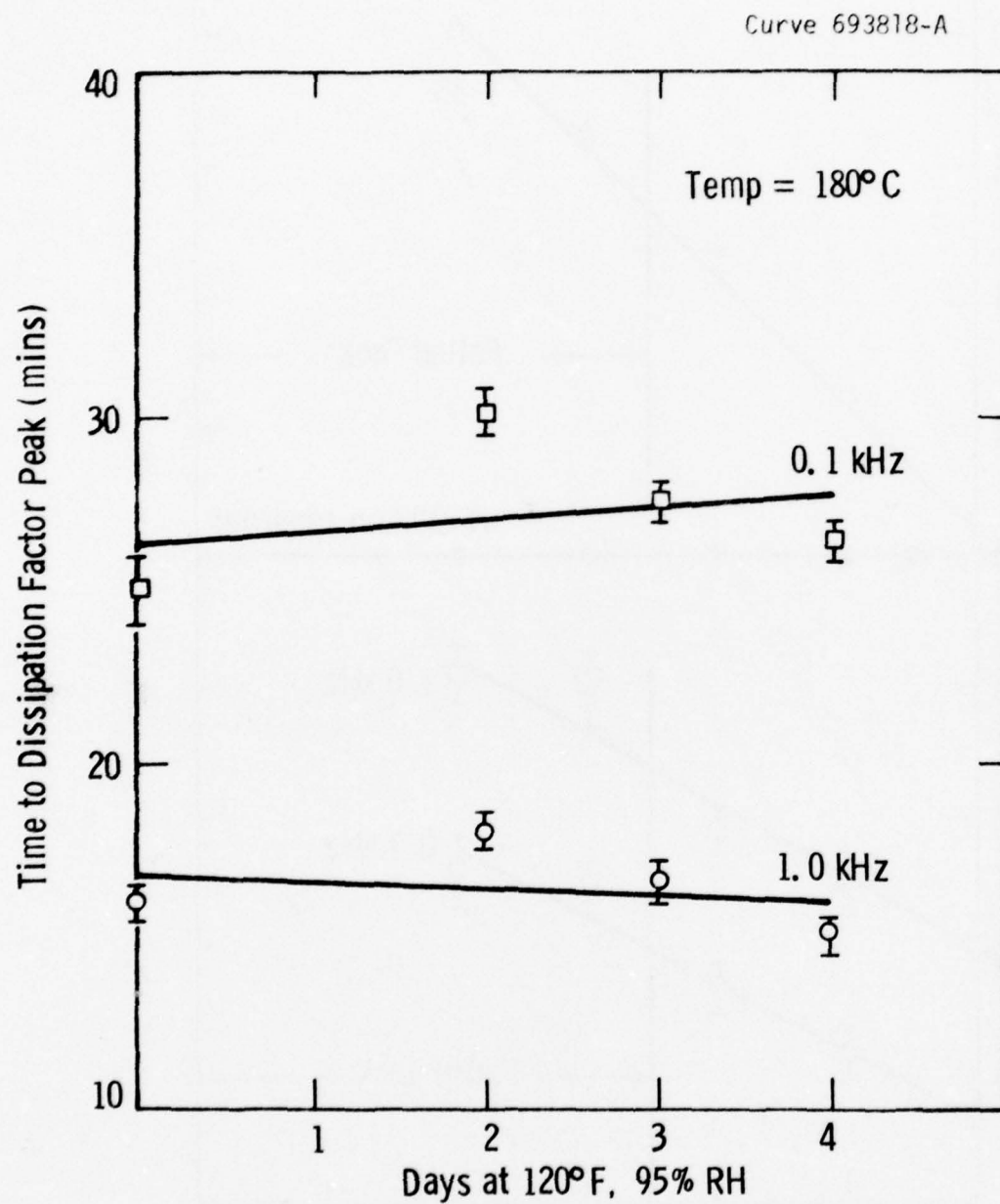


Fig. 20— 120°F 95% RH aging - dielectric analysis, isothermal time to peak data

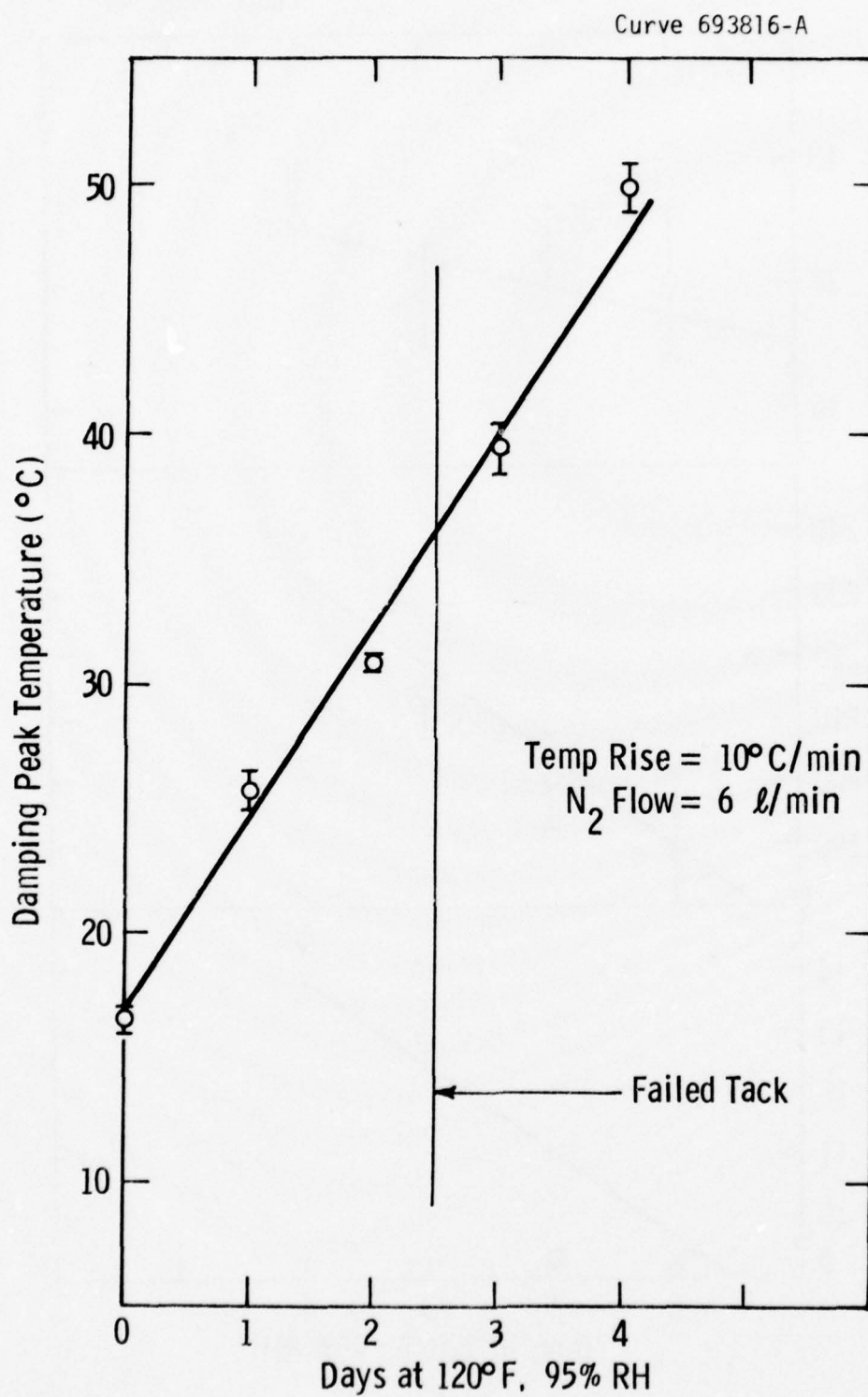


Fig. 21 - 120°F 95% RH aging - DMA data

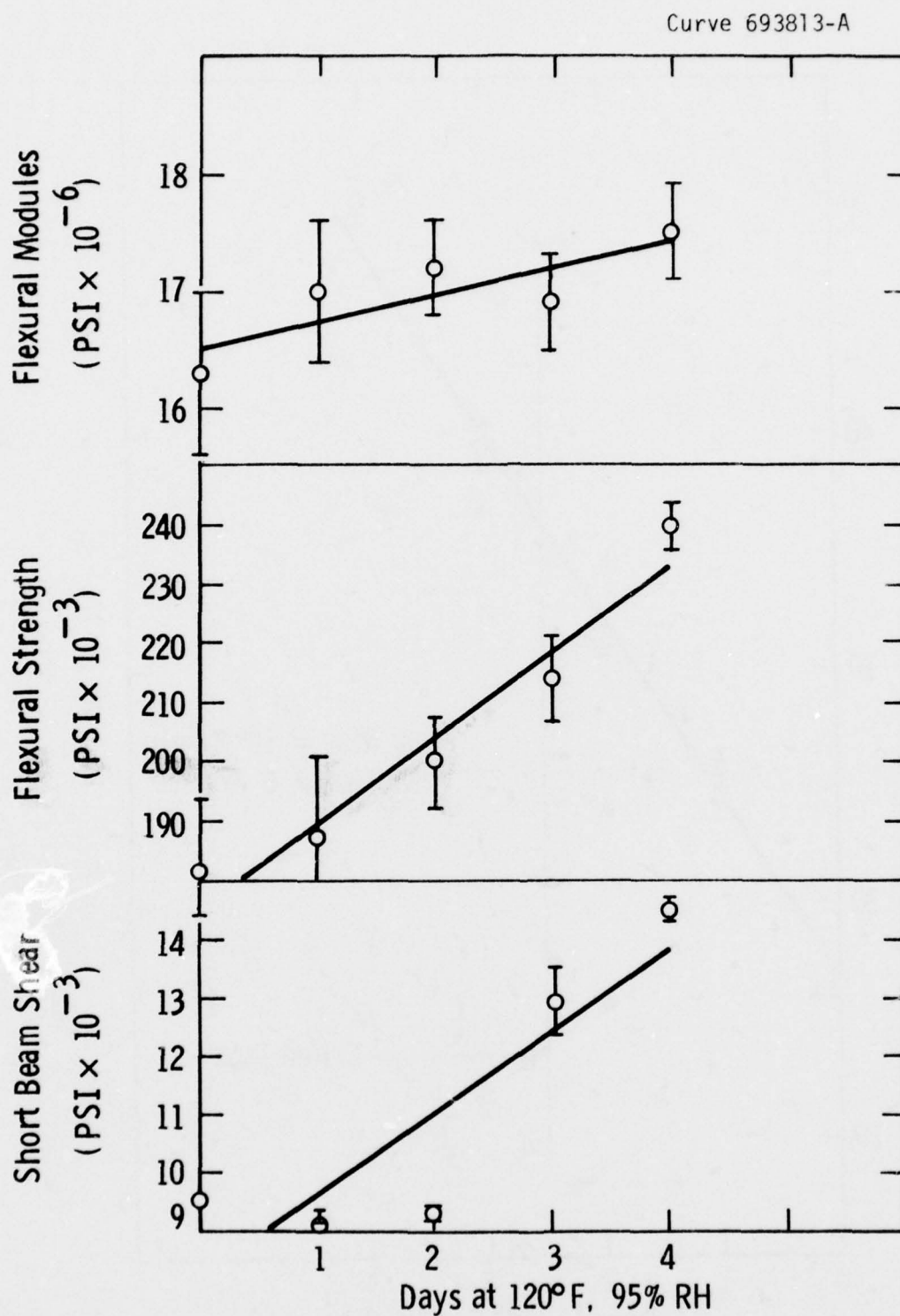


Fig. 22-120°F 95% RH aging - mechanical test data

peak temperature is about 35°C. Figure 16 (top) shows the resin flow diminishing with age, and Figure 22 shows the mechanical test data. The data and the explanation for it is similar to the behavior shown in Figure 18.

Table 5 presents the DSC data and this shows somewhat better trend of declining  $\Delta H$  values with prepreg age, but there is too much variation in the data for it to be useful. As explained in 4.2, the variations are probably caused by local differences in the resin/fiber ratio.

TABLE 5  
120°F, 95% RH AGING - DSC DATA  
AVERAGE OF THREE SAMPLES

<u>Age at Condition (Days)</u>	<u>Peak Exotherm Temp. (°C)</u>	<u><math>\Delta H</math> (Cals/gm)</u>
Fresh	233	31.5
1	238	25.4
2	236	31.1
3	235	26.8
4	234	21.8

#### 4.4 120°F, 80% RH INTERMITTENT EXPOSURE

The purpose of this study was to investigate the effect of a lower humidity than in 4.2 and the effect of cycling the prepreg between the freezer (-4°F) and the exposure conditions. The cycle periods varied according to convenience from 8-24 hours at aging condition and 8 to 72 hours in the freezer.

This was the last (chronologically) aging study made and while the study is complete, the mechanical test data and resin content data are not yet available. The dielectric analysis, and TTW data are presented in Figure 23 and DMA data in Figure 24. This aging study is presented here even though incomplete, because it is the only one performed on the FA batch of material (see Section 3.1) which contains less resin content.

The lower resin content, as expected, results in a somewhat quicker loss of tack (about 2 days). At this point when the prepreg has lost its tack,

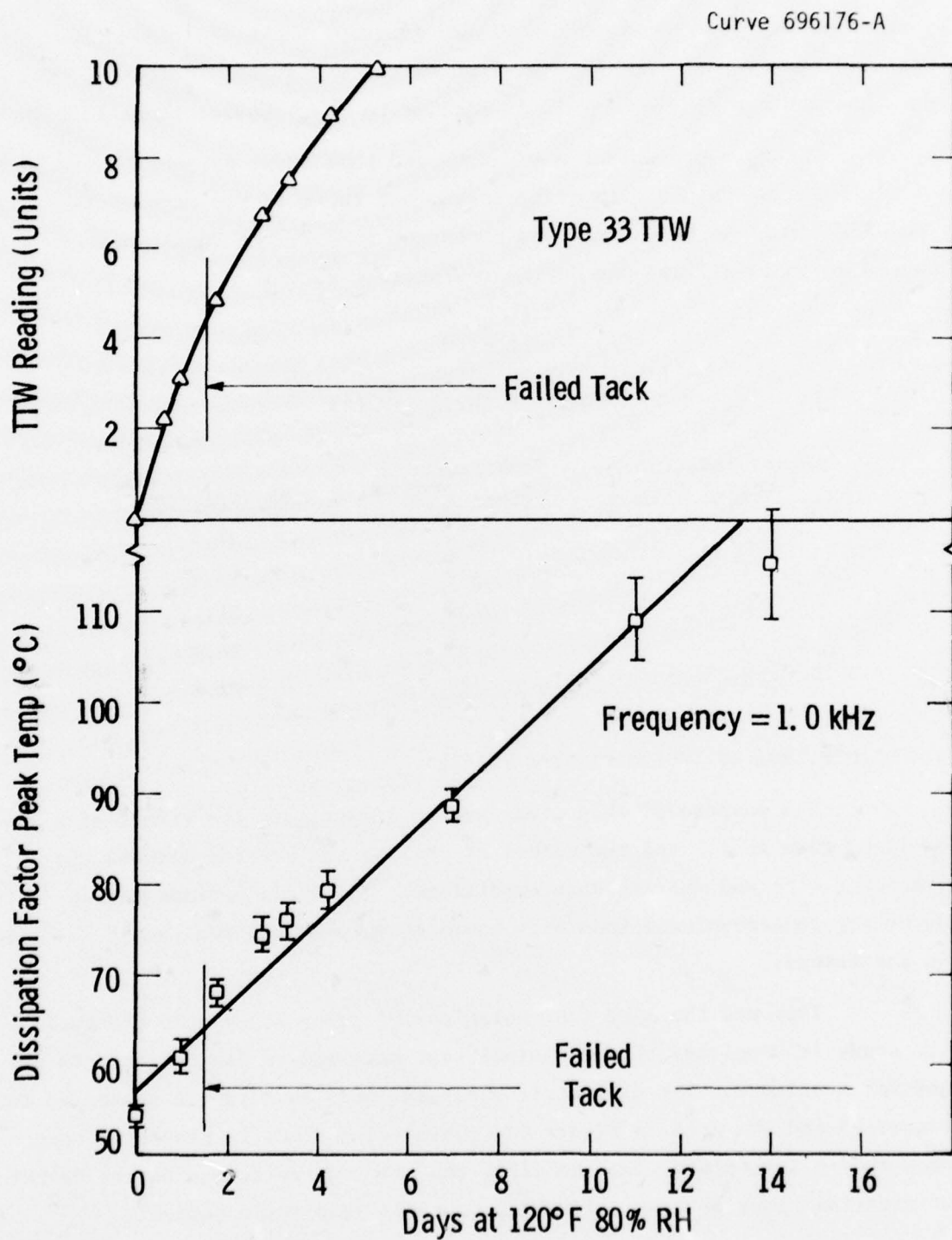


Fig. 23— FA batch, 120°F 80% RH aging - dielectric analysis and TTW data. \*Intermittent exposure from freezer (-4°F) to aging conditions

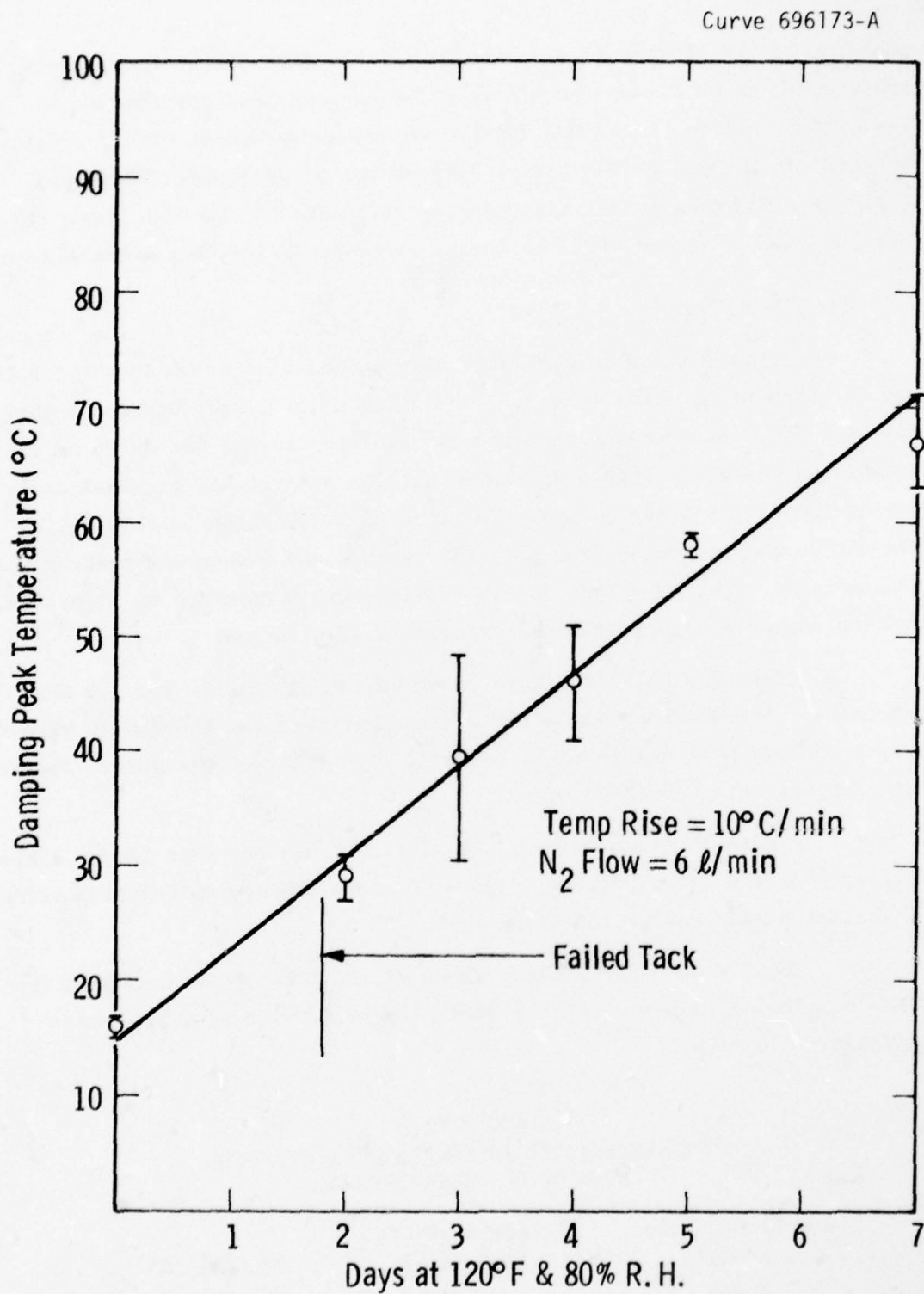


Fig. 24— Intermittent exposure from freezer -4°F to 120°F & 80% R.H. — DMA data

the Type 33 TTW reading is 4.5, the DA 1.0 kHz dissipation factor peak temperature is 63°C, and the DMA relative damping peak temperature is about 30°C. These DA and DMA values are all in agreement with the values obtained at the end of the useful life of the prepreg under 120°F and 120°F, 95% RH aging conditions. As expected (due to the high humidity), the TTW reading agrees with the latter aging condition, but not the former.

#### 4.5 AMBIENT AGING

Ambient aging in the laboratory was carried out with the F batch and FA batch of material (see 3.1). Figures 25, 16, and 26 present the data for the F batch aging when the average temperature was 72°F and the average RH was 62%. Figure 25 shows that the prepreg had marginal tack during the 22 to 30 day period. The Type 33 TTW reading in this period was 4 when the prepreg became marginal in tack and 6 when the prepreg had unacceptable tack. The Type 30 TTW readings are also shown on Figure 25, and its range is clearly too short for this application.

The lower half of Figure 25 shows the DA results for 1.0 kHz frequency. The dissipation factor peak temperature was about 60°C when the prepreg became marginal in tack, and 64°C when all tack was lost. Isothermal time to peak data showed no trend.

Figure 16 (lower) shows the effect of age on resin flow - a slow decline over the aging period. Figure 26 shows the mechanical properties of laminates made during the aging period.

The DSC data for ambient aging of the F batch is presented in Table 6. The  $\Delta H$  values show some declining trend with age, but the variability is high.

TABLE 6  
ROOM TEMPERATURE AMBIENT AGING - DSC DATA  
AVERAGE OF THREE SAMPLES

Age at Condition (Days)	Peak Exotherm Temp. (°C)	$\Delta H$ (Cals/gm)
Fresh	235	35.2
3	230	23.1
13	235	26.9
23	235	16.4

Curve 693809-A

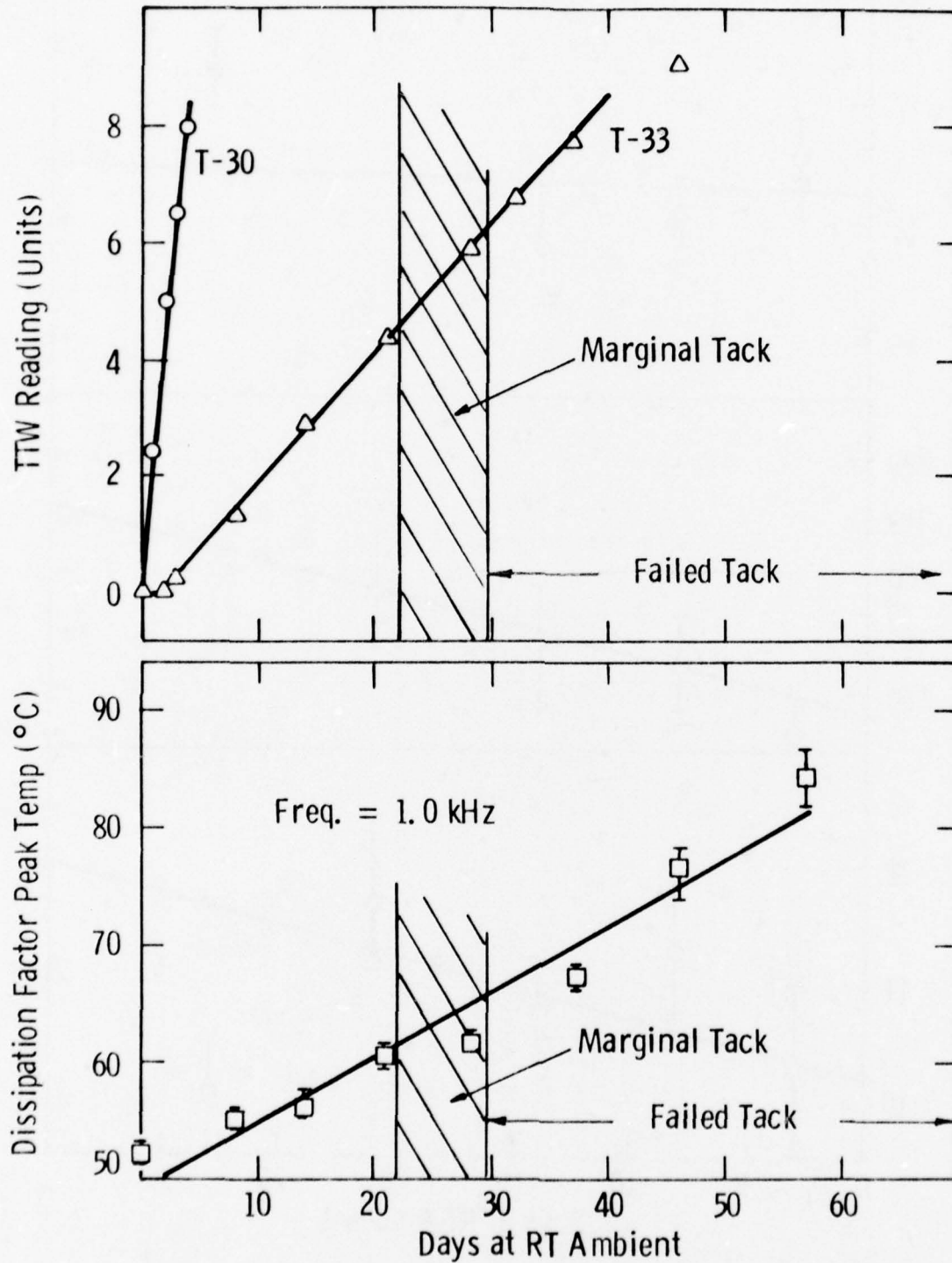


Fig. 25- Room temp aging - dielectric analysis & TTW data  
Avg temp = 78°F Avg RH = 62%

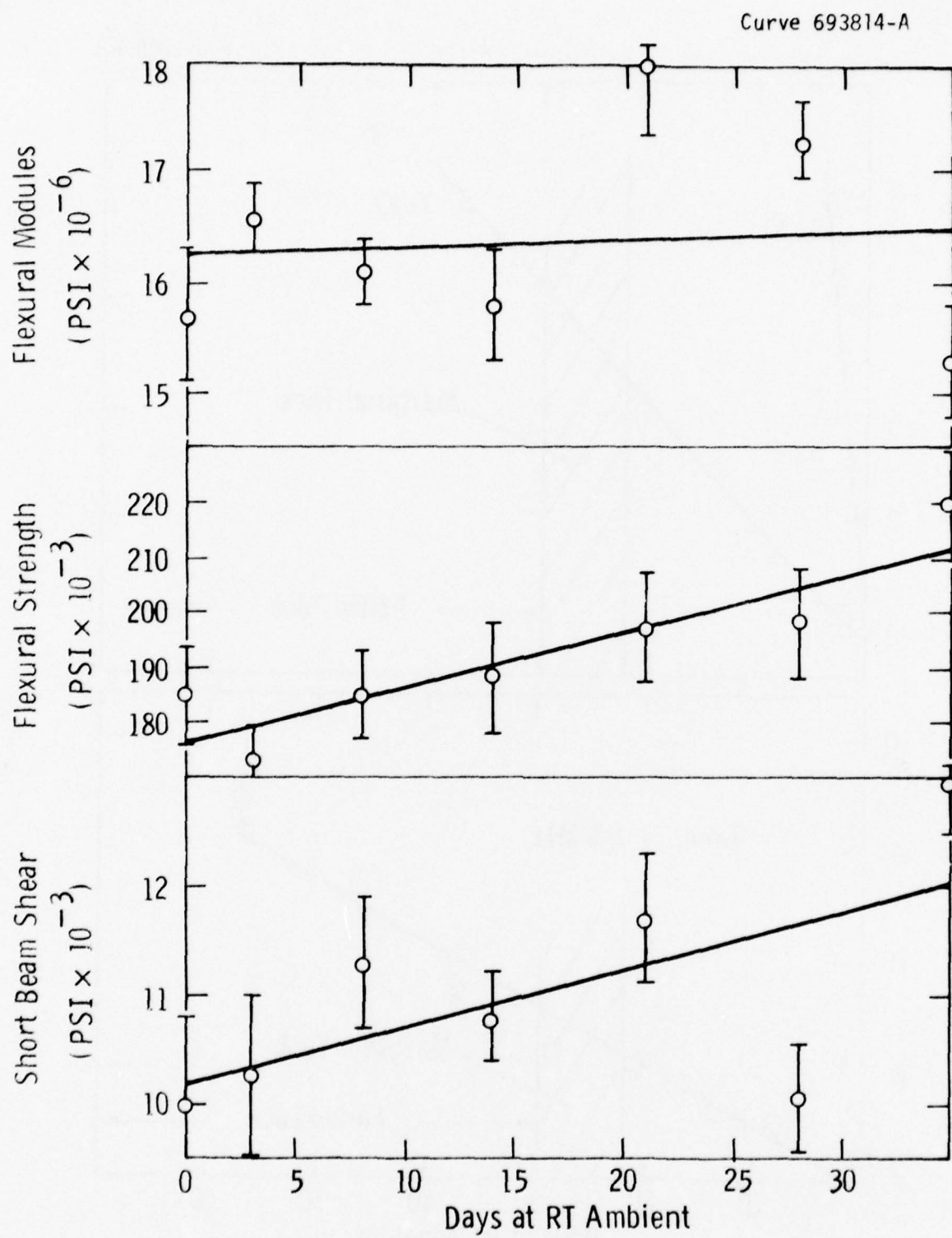


Fig. 26- Room temp aging - mechanical test data

Figure 27 shows the RT ambient aging data (average temperature 72°F, average RH 35%) for the FA batch (lower resin content). It can be seen that as the prepreg begins to loose its tack, the Type 33 TTW reads 3.5, and 5 by the time it has lost its tack. The DA data shows a 1.0 kHz peak temperature at 62°C at the marginal tack point, and 65°C at the end of tack.

The chemical changes taking place during ambient aging can be seen in Figure 12 (and are discussed in Section 3.6).

#### 4.6 FREEZER AGING

The data for freezer aging is presented in Figures 28 and 29. This aging series is still continuing; the prepreg has not lost its tack. Figure 28 shows trends which would indicate that some aging has taken place. The upper part shows resin flow and it has declined from an initial 28% to the present 22%. The dissipation factor peak temperature at 1 kHz has increased from an original 50°C to the present 54-56°C. Some chemical change data on aging in a freezer at 10°F obtained at the AMMRC by G. L. Hagnauer (see Section 3.6) shows a small (1%) reduction of TGMMA and DDS after 41 days at 10°F. Also, the mechanical properties as shown in Figure 29 have the same trend with age as the previously discussed studies - i.e., a small increase with age as the resin squeeze-out diminishes. These would all tend to support the hypothesis that some aging has taken place.

It should be noted that Figures 28 and 29 show data for two batches of prepreg obtained at different times from Hercules, Inc. The circles represent data for the original batch (F) of prepreg obtained in July. The triangles represent data from a second batch (FN) of prepreg which was obtained in November. When it was tested soon after receiving, it was found to give dielectric analysis results showing higher values than the original batch (55°C instead of 50°C). It was then discovered that that batch of prepreg had been made much earlier (August) and had been stored by Hercules in a freezer till it was shipped to us. Using the date of manufacture as the zero point on the time axis, the data for the new batch fell in line with the data for the old batch.

Curve 696174-A

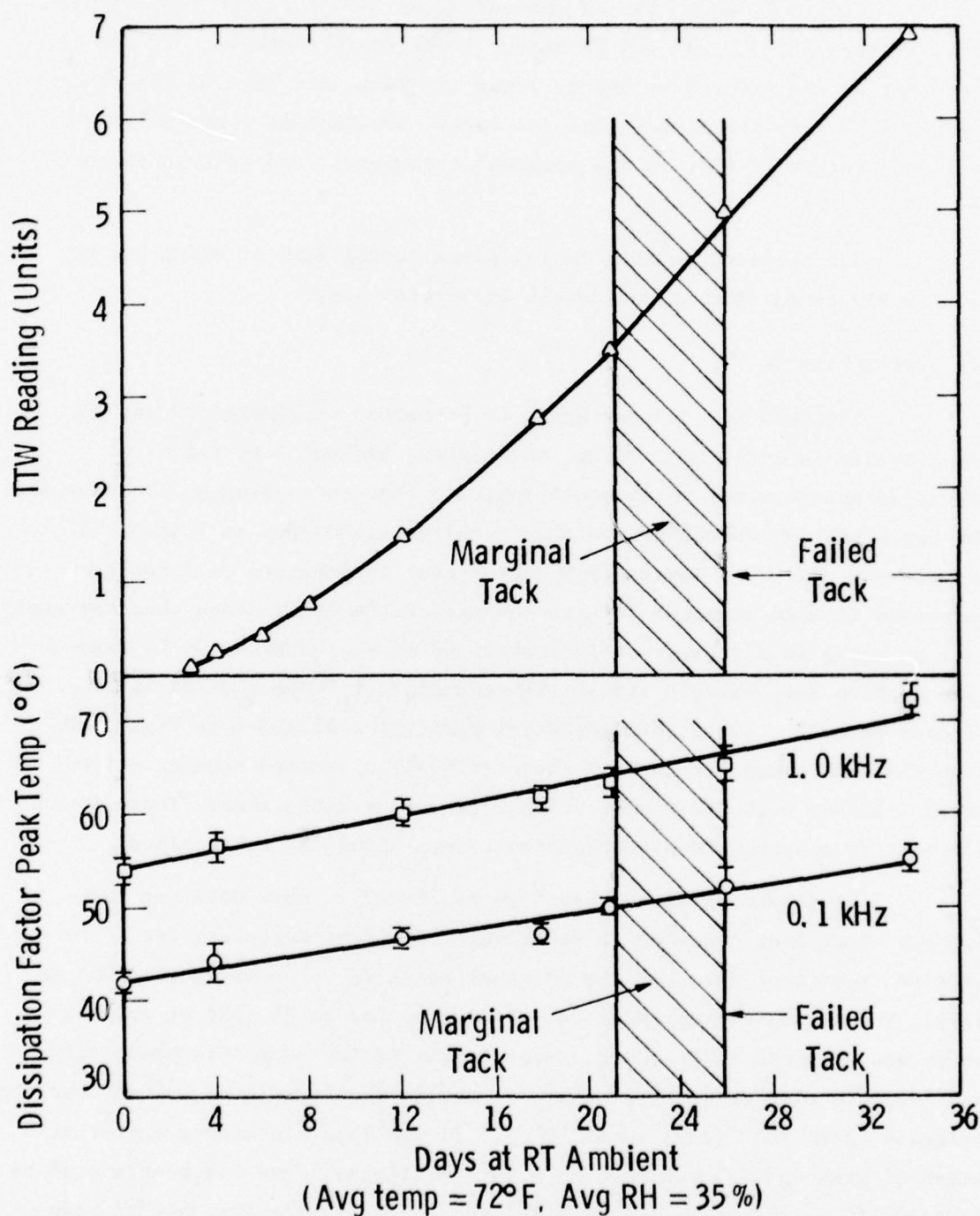


Fig. 27 - FA batch, room temp aging - dielectric analysis and TTW data, intermittent exposure from the freezer (-4°F) to ambient

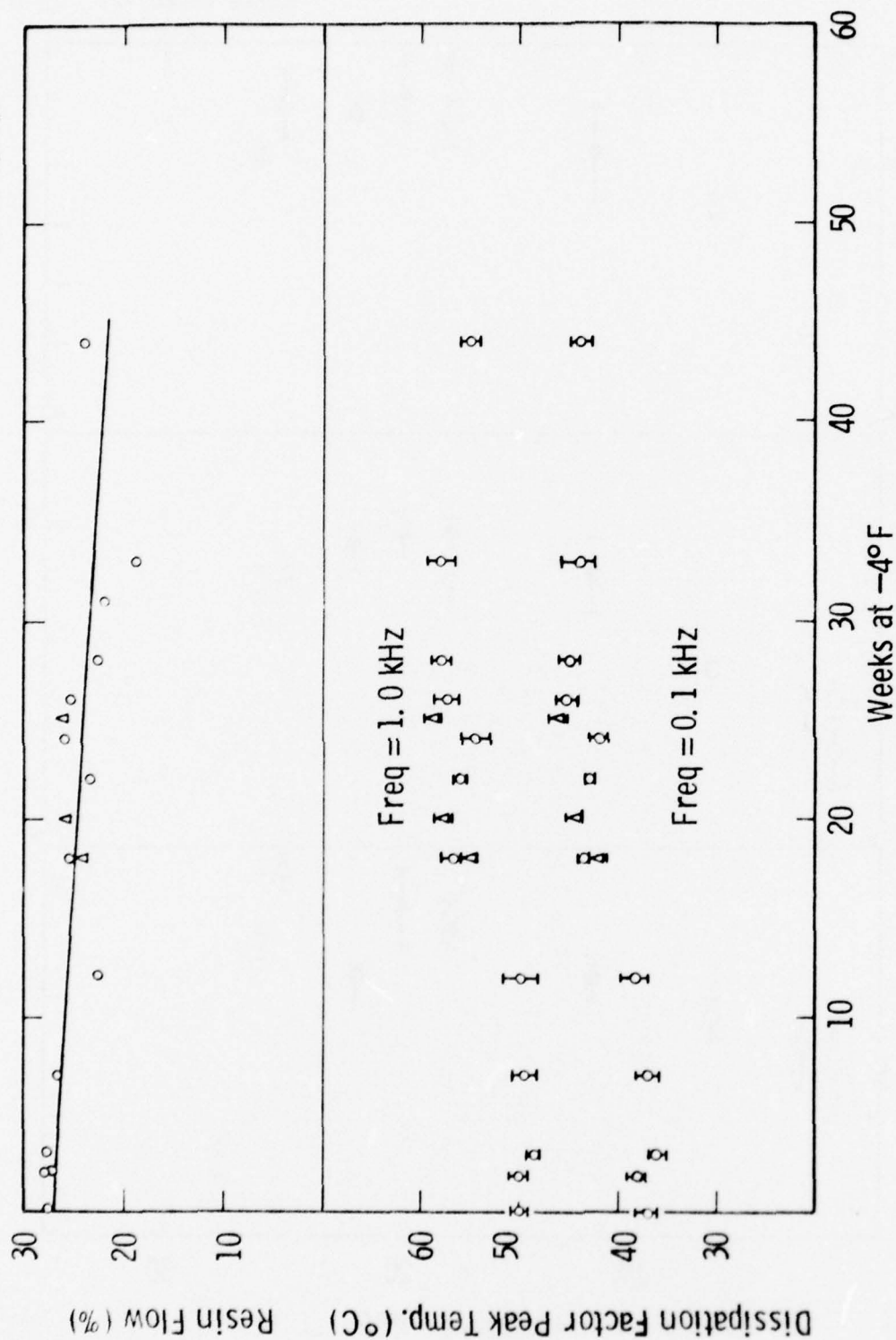


Fig. 28 - Freezer aging, -4°F, dielectric analysis and flow data

○ F batch, △ FN batch

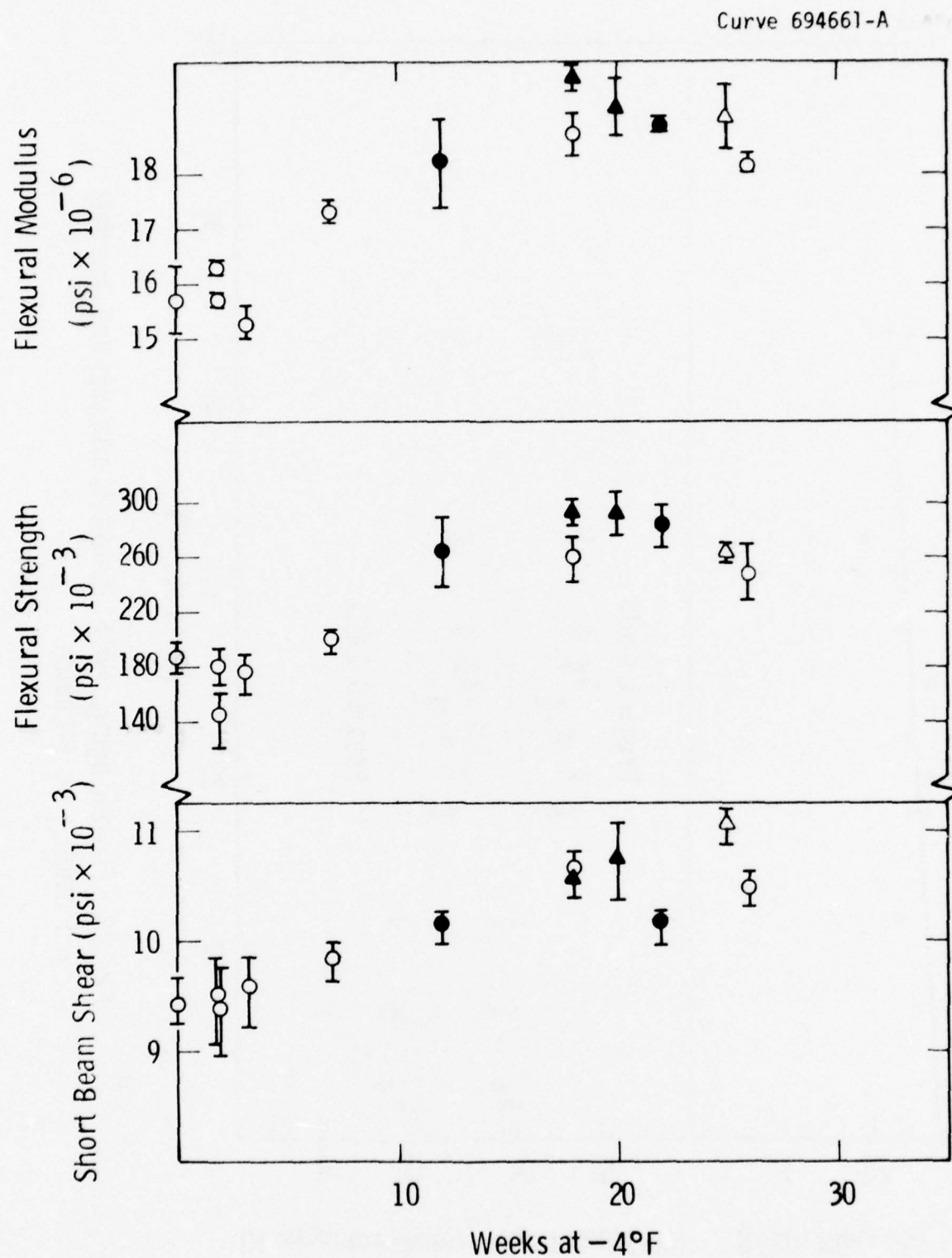


Fig.29— Freezer aging (  $-4^{\circ}\text{F}$  ) - mechanical test data  
 ○ F batch    △ FN batch

The effect of post curing the laminates for 8 hours at 180°C was verified using some of the freezer aged laminates. The filled triangles and circles represent the post cured laminates. There is a marginal increase in flexural strength with post cure. However, there is a marginal decrease in the short beam shear strength. No discernible effect of the post cure could be noted on the flexural modulus values. While laminates have been made at periods beyond the 26 weeks shown, these are awaiting testing.

The DA data of Figure 28 is somewhat puzzling because most of the change appears to have taken place in the 12-20 week period. This could be due to: (1) actual aging change at -4°F, (2) a malfunction of the freezer or inadvertant removal of the prepreg container for several hours, or (3) an environmental condition that affected the test results (such as lower humidity in the winter). The resin flow, mechanical property, and chemical analysis data would lend support to the conclusion that an actual change had taken place due to (1) or (2).

The freezer aging study points to a potential problem with the use of the TTW. The Type 33 shows no reading at all after 45 weeks in the freezer (-4°F). The Type 33 will not respond at such a low temperature and thus any aging taking place in the freezer will not be recorded by the Type 33 TTW. The seriousness of this would depend on the amount of aging taking place in the freezer. This will be verified after the 52 week freezer aging is complete by subjecting the aged prepreg to an ambient aging test.

It should be noted that there are other TTWs that respond at -4°F. The Type 21 and 27 are fairly rapid at this condition and not suited (without modification) for a 1 year exposure at -4°F. The Type 30 has the right range for this application. After 45 weeks at -4°F, it shows a reading of  $\sim 2$ . It could be considered for use in conjunction with the Type 33 or alternatively, the prepreg can be discarded after 1 year storage in the freezer, regardless of the reading shown by the Type 33.

#### 4.7 SUMMARY OF AGING STUDIES WITH 3501-6/AS PREPREG

The aging studies have shown that under different aging conditions, several methods can be found that can reliably track the age of the prepreg

and can give a test value (called here the critical value) which can be used to determine when the useful life of the prepreg is over. In our studies, the value of the age indicating test was correlated to the loss of prepreg tack. It is also possible to obtain a value which would correlate with the loss of some other property if that property is considered more critical.

The age indicating methods, the critical value obtained with the 3501-6/AS prepreg, and the relative merits are discussed below:

- Time Temperature Watch: This type of time temperature integrator was found to be quite accurate. Within limited ranges of temperature, it was able to indicate when the prepreg would loose its tack. Depending on the humidity, this critical value is between 4 to 6 units for the Type 33 TTW. Its chief merit lies in its simplicity of use and low cost. It is ideally suited for use where other more technically elaborate methods cannot be used. It has to be carried with the prepreg at all times. While its readings are slowed down by high humidity exposure, the change appears not critical for this application. Where critical, the packaging can be improved to overcome or reduce this effect.

- Dielectric Analysis: This method can accurately follow the aging of the prepreg and correlate the value of a property with the loss of tack. The property is the temperature of the peak in dissipation factor at 1 kHz. Using our sample configuration and heat-up rate, this was found to be  $62^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . Isothermal methods were not as successful, and the only problem encountered was the effect of humidity which can be overcome by drying the samples prior to test.

- Dynamic Mechanical Analysis (DuPont 980 DMA): This method is quite accurate and sensitive provided the experimental conditions (including thermocouple location) are kept absolutely identical each time. The property that correlates well with prepreg age is the temperature of the relative damping peak. The critical value was found to be  $32 \pm 3^{\circ}\text{C}$ .

• Chemical Separation and Analysis: A limited amount of work done elsewhere indicates that reverse phase liquid chromatography coupled with Fourier transform infrared analysis can successfully indicate the chemical changes associated with the aging of the prepreg.

• Differential Scanning Calorimetry: In our studies, this method was unsuccessful in following the age of the prepreg. A good correlation was found neither between the temperature of the peak exotherm and prepreg age nor the exotherm and prepreg age. Work reported in the literature indicates that for some prepreps and resins, this might be an appropriate method.

## 5. CONCLUSIONS

1. Several methods exist which can follow the aging of a thermoset resin mixture (such as in a prepreg product) and can indicate when the product is overaged.
2. Three of the methods examined depend upon obtaining a response from the material. The response then changes monotonically with time as the chemical reactions causing the advancement of the resin take place as a function of time and temperature.
3. These three are dielectric analysis, dynamic mechanical analysis, and differential scanning calorimetry.
4. Of the three, dielectric analysis and dynamic mechanical analysis were found to be accurate and sensitive indicators of prepreg age. Both methods provided a value which would indicate the prepreg (Hercules 3501-6/AS) had reached a critical or overage condition.
5. Differential scanning calorimetry was not completely successful in tracking the age of the 3501-6/AS prepreg. There were some trends with age but the responses varied too much to provide a critical value, which might be used to indicate an overage condition.
6. Chemical analysis methods, particularly reverse phase liquid chromatography coupled with Fourier transform infrared analysis may also be used to track prepreg age.
7. A practical, easy to use and inexpensive method that correlates well with prepreg age (within limited temperature ranges) was also found. This is a device which provides a reading corresponding to integrated time and temperature of exposure and is called a Time-Temperature Watch.
8. Such devices perform no test on the material and are therefore ideally suited for field and on-board ship use where test facilities may not be present. However, they do have to be carried with the material at all times.

## 6. RECOMMENDATIONS

1. Effort should be continued to further characterize the behavior of the Type 33 TTW by performing aging studies at other temperatures and humidities.
2. Another time-temperature integrating device - 3M Co.'s Monitormark - should be studied under diverse aging conditions with the 3501-6/AS prepreg.
3. Aging studies should be performed on the 3501-6/AS prepreg with known small changes in chemistry. The purpose of this would be to determine the effect (if any) of chemical changes on the aging of the prepreg and the age indicating methods.
4. Some effort should be devoted towards improving the packaging of the time-temperature integrating devices to increase their humidity resistance.
5. Aging studies should be initiated on other prepregs and adhesives of interest.

## 7. REFERENCES

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APPENDIX A

TIME/TEMPERATURE WATCH

A.1 - THE INFO-CHEM TIME/TEMPERATURE WATCH™

PRODUCT DESCRIPTION

The INFO-CHEM TIME/TEMPERATURE WATCH™ is a means to record the time/temperature conditions to which a product is subjected during storage, shipping and handling. If properly adapted to simulate the degradation characteristics of the product, it also indicates the condition of the product at any point of the distribution chain.

The TIME/TEMPERATURE WATCH™ is a 7x1 inch flexible plastic device. It has a sensing part and a recording part, like a thermometer. It is started by breaking the tiny glass ampule incorporated at the sensing end. Activation starts the release of a small amount of a chemical that will record time. An activation dot will turn color within a few seconds proving that the time clock is put in motion.

The recording part consists of a 3.5 inch window showing a colored strip with a 1 to 10 linear scale. With time, the scale will color. The length of the color change will be a direct measure of integrated time/temperature exposure. Namely, the time clock will run faster at a higher temperature.

The wide bar and sharp front make the indicator easy to read, even from a remote distance. A pressure sensitive adhesive on the back of the indicator facilitates its application to the outside of a case or pallet. Alternatively, the TIME/TEMPERATURE WATCH™ can be enclosed in the case, should the user not want the time/temperature information known, until it reaches the end of the distribution chain.

### THE TIME/TEMPERATURE CONCEPT

The quality or shelf-life of many products is affected by time and temperature.

At a constant temperature, time effects are linear. If a product has a shelf-life of two years at 80°F (27°C), half of that life will be lost after one year. Temperature effects, however, are exponential and a shelf-life of two years at 80°F (27°C) could shrink to a mere 11 days at 140°F (60°C). Keep in mind that 140°F (60°C) temperatures can be reached in a closed space, such as a truck, when exposed to the sun (see the graph on the next page).

The TIME/TEMPERATURE WATCH™ can simplify control by providing a simple means to determine, analyze and correct weaknesses in handling, storage, and stock rotation practices. Furthermore, with the aid of the TIME/TEMPERATURE WATCH™, products which have been subjected to thermal abuse within the distribution chain can be readily identified and withdrawn before reaching the market. Examples would be biologicals, diagnostic reagents, plasmas, and hospital solutions, all of which are known to be very sensitive to temperature fluctuations. However, even products that are quite stable at normal ambient conditions, require monitoring during uncontrolled transportation. The TIME/TEMPERATURE WATCH™ can also be used in raw material storage.

A.2 - TIME/TEMPERATURE WATCH ACTIVATION

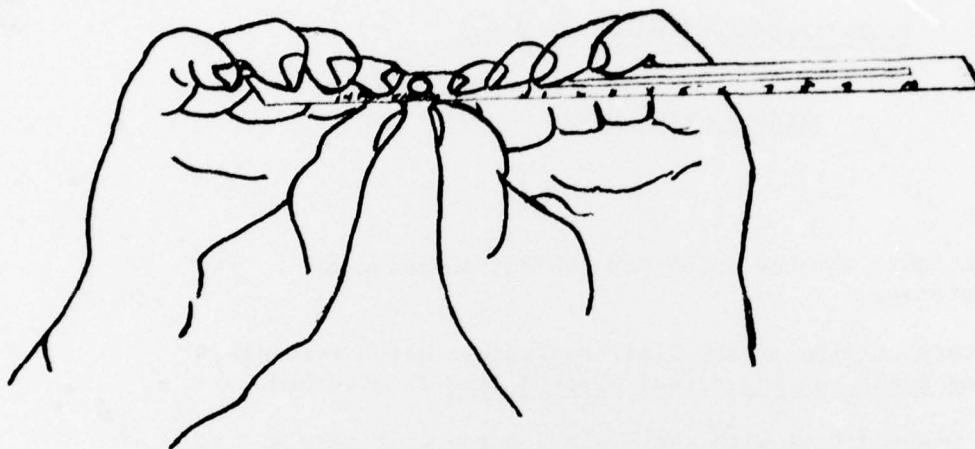
Proper activation is very important for the correct functioning of the Info-Chem Time/Temperature Watch.

The Time/Temperature Watch is activated by gently breaking the tiny glass ampul housed directly under the activation dot. The ampul is contained in a strong Tyvek pouch to prevent damage. Nevertheless, rough activation could permanently damage the release mechanism. As a result, the Time/Temperature Watch may run too fast.

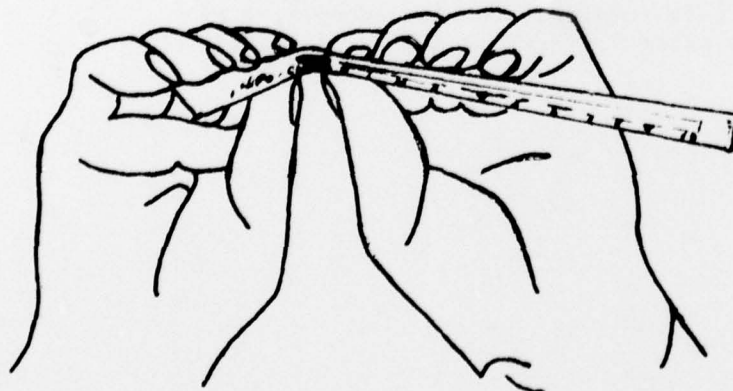
We recommend you carefully follow the instructions for activation of the Time/Temperature Watch.

INSTRUCTIONS FOR ACTIVATION OF THE  
INFO-CHEM TIME/TEMPERATURE WATCH (TTW)

- STEP 1. PLACE THUMBS AND INDEX FINGERS ON BOTH SIDES OF THE ACTIVATION DOT.



- STEP 2. BEND GENTLY UNTIL YOU HEAR AMPUL SNAP.



- STEP 3. A COLOR CHANGE OF THE ACTIVATION DOT SHOWS THAT ACTIVATION OCCURRED. THIS MAY TAKE SOME TIME, ESPECIALLY WITH LONG TERM TIME/TEMPERATURE WATCHES.

A.3 - TIME/TEMPERATURE WATCH TYPE #33

READING PROCEDURE

Type #33 is designed for use in either ambient shipping or refrigerated storage.

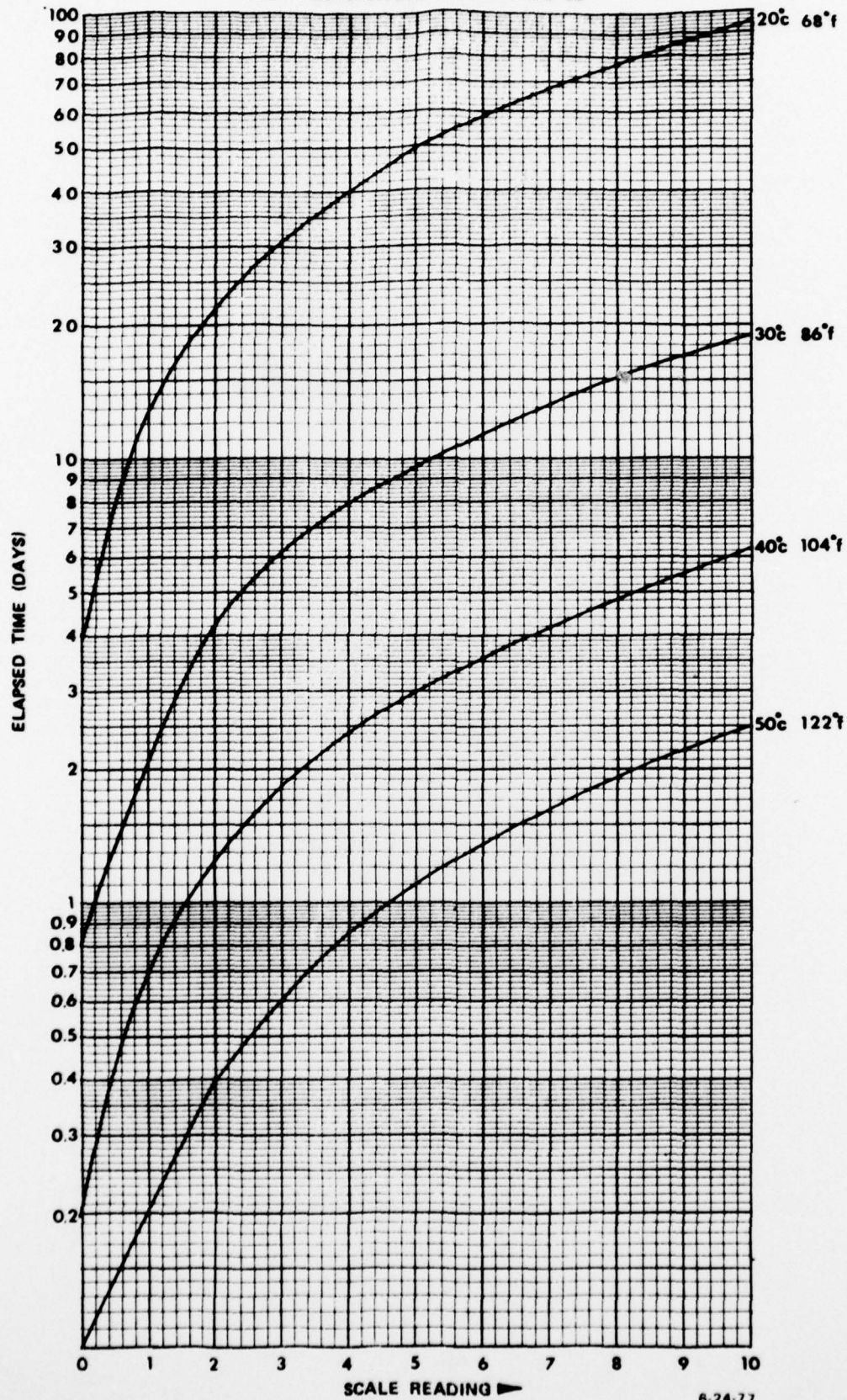
For simple interpretation of the Time/Temperature Watch readings, a graph showing scale reading versus elapsed time is attached.

Combining the elapsed time with the scale reading will give a point on this graph. For example, a scale reading of 5 after 9.6 days shows that the average effective temperature was 30°C or 86°F.

If the product should not be exposed to temperatures above 30°C, the area of the graph on the left hand side of the 30°C line can be marked safe. This means that safe readings are, for example, 2 or less after 4.2 days, 5 or less after 9.6 days, and 8 or less after 15 days.

7/14/77

# TIME TEMPERATURE WATCH TYPE 33



APPENDIX B

PREPREG TACK TEST  
AND  
PREPREG RESIN FLOW TEST

(Reproduced from Hercules, Inc. Graphite  
Composite Testing Procedure HD-SG-2-6006C)

5.4 Tack test. The prepreg tack test shall be performed as follows:

5.4.1 Test specimens. The test specimen shall consist of two - 2 inch by 2 inch prepreg squares.

5.4.2 Test procedure. The test procedure shall be as follows:

- a. Clean the surface of a vertically mounted stainless steel plate using MEK or acetone. Make sure the solvents are not contaminated.
- b. Remove any film left by evaporation of the degreasing solvent with a chlorine-free scouring powder and either distilled or demineralized water, then allow to dry at room temperature.
- c. Make a straight line with a greaseless marker across the plate as shown in Figure B-1.
- d. Remove release paper from one side of the specimen then apply the side of the specimen from which the release paper was removed to the plate with the line at the bottom of the specimen. With light up and down motion use the fingers to smooth out creases and wrinkles. All specimens are to be mounted while plate is in vertical position.
- e. If present, remove plastic film from specimen applied to plate in step d, then remove release paper from a second specimen. Note that fibers of both patches are to be oriented on the plate in a vertical fashion.
- f. Place second specimen on top of specimen on plate as described in step d and Figure B-1. Upon application of the second specimen, start a timing device to monitor test.
- g. No motion of the specimen for a minimum period of 30 minutes constitutes a tack test which passes.
- h. Run two tests in accordance with steps d through g unless otherwise specified. A successful tack investigation is one which all specimens tested pass.
- i. After completion of the tests, remove the prepreg squares from the plate and immediately clean the plate in accordance with steps a and b.

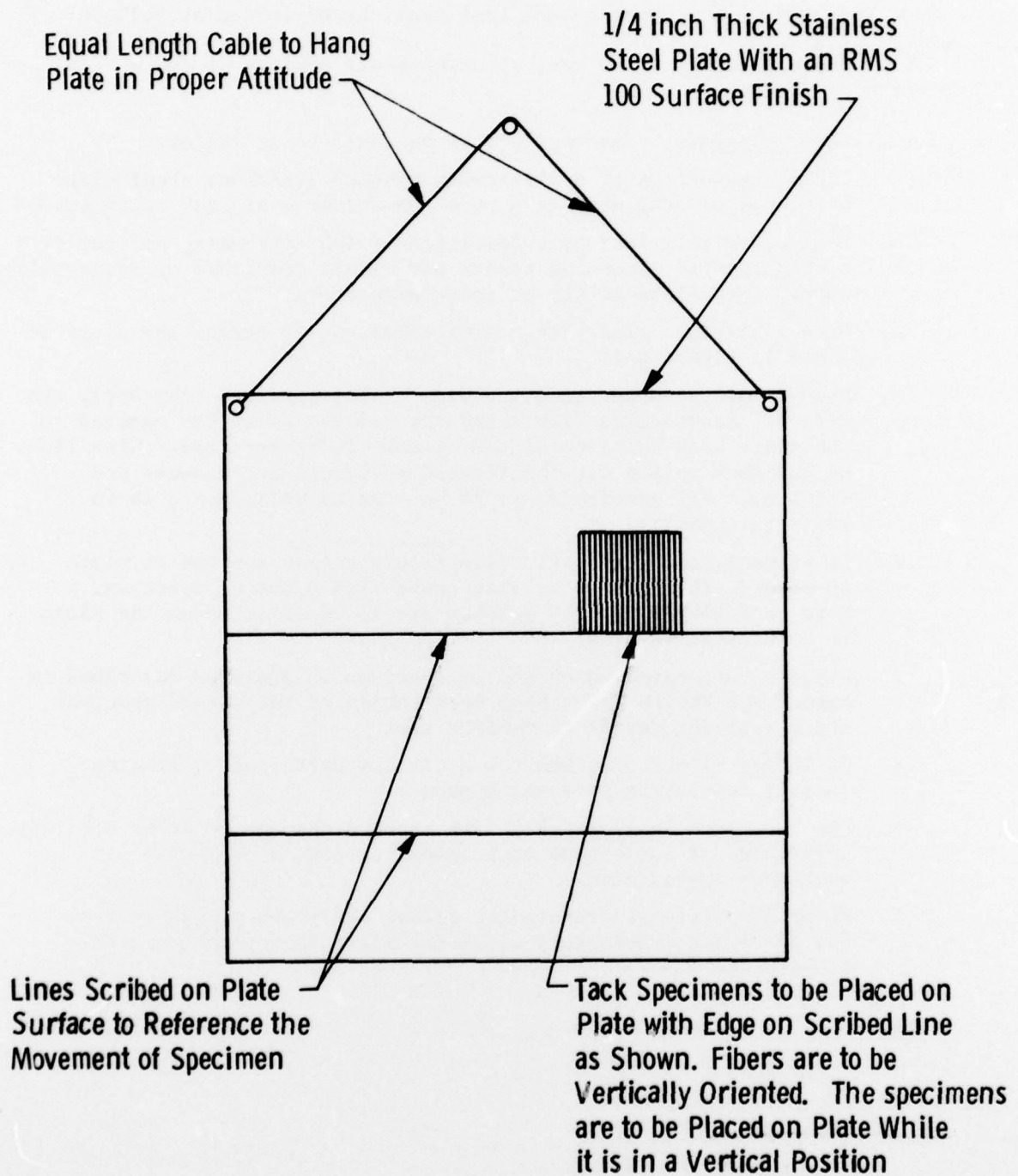


Fig. B-1 - Tack test set-up

5.3 Resin flow. The resin flow properties of the prepreg shall be determined in accordance with procedure A or procedure B as specified in the applicable prepreg specification sheet.

5.3.1 Procedure A. Determine resin flow as follows:

- a. The test specimen shall consist of two uniformly cut pieces of prepreg. Each piece shall be 2 inch by 2 inch.
- b. Cut four approximately 3-inch squares of glass bleeder cloth for each test.
- c. Cut two approximately 3-inch squares of porous tetrafluoroethylene (TFE) release cloth.
- d. Cut one approximately 6-inch by 12-inch piece of aluminum foil.
- e. If the prepreg has release paper on both sides, remove the release paper from one side of each of two 2 x 2 inch specimens.
- f. Sandwich the exposed sides of the graphite together so that the fibers are oriented 90 degrees to each other. Then remove the release paper from one side of the specimen sandwich.
- g. Weigh the sandwiched specimen to the nearest milligram on a precision balance. The side of the sandwiched specimen with the release paper attached is to be placed on the balance pan. Record the weight as  $W_1$ .
- h. Fold the 6 x 12 inch sheet of aluminum in half to form a 6 x 6 inch square. Then unfold and lay on a flat surface.
- i. Stack two pieces of the fiberglass bleeder cloth on one another and lay them on top of the aluminum foil aligning one edge with the center crease of the foil.
- j. Center one piece of release cloth on top of the bleeder cloths.
- k. Center the exposed side of the prepreg specimen on top of the release cloth.
- l. Remove the final piece of release paper from the specimen and weigh the release paper to the nearest milligram. Record the weight as  $W_2$ .
- m. Center one piece of TFE release cloth on top of the fresh/posed graphite surface of the specimen; then place two pieces of bleeder cloth on top of the release cloth.
- n. Fold the aluminum foil over to form a 6 x 6 inch square completing the sandwich lay-up.
- o. Pre-set the temperature of the platen press to the temperature specified in the applicable prepreg specification sheet and check.
- p. Place the sandwiched specimen on the top platen of the press and immediately (within 15 seconds) apply the pressure specified in the applicable prepreg specification sheet to the specimen. Start a timer when the required pressure is obtained.

- q. Remove the specimen from the press after the time specified in the applicable prepreg specification sheet has elapsed. Allow specimen to cool to room temperature.
- r. Remove the graphite specimen from the lay-up. Insure that no fibers are removed with the release cloth.
- s. Remove any resin which has extruded from the body of the graphite specimen and is clinging to the edges.
- t. Re-weigh the graphite specimen to the nearest milligram. Record weight as  $W_3$ .
- u. Calculate the percent resin flow as follows:

$$\text{Resin flow, percent} = \frac{(W_1 - W_2) - W_3}{W_1 - W_2} \times 100$$

where:  $W_1$  = initial weight of specimen plus one piece of release paper, g.

$W_2$  = weight of release paper from  $W_1$ , g.

$W_3$  = final weight of specimen, g.

- v. Report individual results of two determinations and also mean value.

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